INVESTIGATIONS INTO GLOW DISCHARGE PLASMAS AS ATOMIZATION
AND EXCITATION SOURCES FOR ANALYTICAL ATOMIC SPECTROMETRY

by

VICTOR PAVSKI, B.Sc, M.Sc.

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the Faculty of Graduate Studies and Research
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AND EXCITATION SOURCES FOR ANALYTICAL ATOMIC SPECTROMETRY"

submitted by

VICTOR PAVSKI, B.Sc. M.Sc.

in partial fulfilment of the requirements
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Chair, Department of Chemistry

Thesis Co-Supervisor

Thesis Co-Supervisor

External Examiner

Carleton University

ABSTRACT

Two complementary atomic spectrometric sources utilizing glow discharges for analyte atomization/excitation were investigated to better understand their fundamental operation so that improvements in their design and operation might result. The first source, a glow discharge atomizer operating in argon at low (1-20 torr) pressure, was characterized for the direct analysis of solid samples by cathodic sputtering. Changes in atomic absorbance and emission signals were measured as atomizer pressure, argon flow rate and discharge power were varied to determine an optimal operational regime for analytical measurements. Self-absorption and self-reversal of commonly-used resonance analytical lines was problematic at all flow rates and degraded performance began in emission at flow rates in excess of 0.5 L min^{-1} .

Line profiles and gas kinetic temperatures were then measured for commonly-used analytical transitions for this glow discharge atomizer and for commercial hollow cathode lamps. A strong similarity in gas kinetic temperatures for both of these sources suggested that analytical calibration curves constructed using these lines will exhibit deviation from linearity earlier than when thermal atomization sources are used.

The second source studied was an atmospheric pressure glow discharge formed in a graphite furnace, termed Furnace Atomization Plasma Emission Spectrometry (FAPES). In FAPES, a helium plasma is formed around a 1-mm diameter graphite rod (which is co-axially centred within a graphite tube) to which radio-frequency (rf) power is applied. The graphite furnace is used to thermally desorb analytes from its surface into the plasma

where they are excited, enabling simultaneous multielement analysis with small-volume liquid samples. Two-dimensional imaging of this source with a charge-coupled device (CCD) camera revealed the existence of a second region of plasma close to the tube wall. The centre electrode acts as an efficient site for condensation and secondary re-vaporization of analyte atoms. Altering the dc bias potential of the centre electrode changed the radial distribution of analytes, suggesting that the rf voltages developed are an order of magnitude lower than previously believed. Easily-ionized elements (EIEs) suppressed the radial emission distribution of Cu and Ag probably because of more efficient loss of photons from the plasma through EIE excitation/ionization.

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INTRODUCTION

Direct analysis of samples in their original form is a worthy goal for any analytical technique. Currently, the majority of commonly-used analytical techniques require the sample to be present in a liquid form, necessitating digestion of solid samples. Of the available techniques for the analysis of solid materials some, such as x-ray fluorescence, have limited sensitivity and require alteration of the form of the sample (*i.e.*, through fusion and the preparation of pellets), thus precluding depth-profile analysis. Others such as arcs, sparks and laser ablation, can suffer from significant problems of matrix effects, stability, or precision and are limited for multielement analysis in the sense that volatilization rates of the analyte elements differ by many orders of magnitude. Although effort has been directed to use more "conventional" analytical sources for solids analysis, such as the graphite furnace [1], these are complicated by the need to carefully microweigh small amounts of the solid sample and have limited throughput capabilities.

Cathodic sputtering in a glow discharge is being increasingly investigated as a means of solid sample ablation [2-5] in an effort to overcome the limitations of the techniques mentioned above. Glow discharge plasmas are being used increasingly for direct solids elemental analysis with a variety of analytical atomic spectroscopic techniques including atomic absorption, emission, fluorescence and mass spectrometry [6-19]. This increased attention undoubtedly stems from their excellent operational stability, relatively simple spectral background and the similar sputtering rates shared by numerous elements [20] which permit refractory and non-refractory elements to be atomized efficiently from

the same sample under the same set of experimental conditions. Furthermore, the components of the sample are sputtered nearly stoichiometrically, producing a plasma whose composition accurately reflects that of the bulk sample [21]. These features suggest that glow discharge sources should afford greater freedom from matrix interferences than thermal ablation techniques such as arcs or sparks [22]. The use of radio-frequency (rf) power has expanded the scope of direct current (dc) glow discharge methods beyond electrically conductive materials by permitting insulators such as ceramics, glasses and polymers to be sputtered directly [2].

Emission techniques offer reasonably cost-effective and rugged means of achieving simultaneous multielement analysis. Currently, the inductively-coupled plasma (ICP) is perhaps the most popular source utilized for this. Most emission techniques employ solution nebulization as a means of sample introduction which has limitations in sensitivity due to dilution of the sample and the low efficiency of solution nebulization. By contrast, the graphite furnace utilizes small (μL) sample volumes, converts nearly all of this sample into atomic vapour and greatly increases the residence time of atoms from ~ 1 ms (solution nebulization) to 1-3 seconds.

A limitation to commercial graphite furnace technology is its inadequacy for simultaneous multielement analysis. Thermal heating of the graphite tube wall is suitable only for emission determination of elements having excitation energies of less than 4 eV (*i.e.*, primarily to elements having spectral transitions above 300 nm) [23]. Transition metal analysis with the graphite furnace is usually accomplished by measuring atomic absorption of radiation from a hollow cathode lamp, which essentially restricts the

technique to sequential single-element analysis. Although four commercial instruments are currently available which afford simultaneous multielement absorption analysis (Hitachi Instruments, Inc. Z-9000; Perkin-Elmer Corporation SIMAA 6000; Thermo Jarrell Ash Corporation AA Scan 4; and Leeman Labs Analyte 5), all utilize combinations of hollow cathode lamps as sources, which restrict their multielement capability to 4-6 elements at a time.

Multielement atomic absorption analysis may potentially be achieved more fruitfully with a technique known as Simultaneous Multielement Atomic Absorption with a Continuum source, or SIMAAC [24,25]. This system utilizes a 300 W xenon arc lamp as a primary radiation source, a high-resolution échelle spectrometer to provide wavelength selection and photomultiplier tubes (PMT) for detection. In such an arrangement, limits of detection are obtained which are comparable to conventional graphite furnace atomic absorption spectrometry (GFAAS) for analysis lines above 280 nm. Limits of detection become increasingly poor at shorter wavelengths, however. Improvements have been realized by replacing the photomultiplier tube with a solid state detector such as a linear photodiode array (LPDA) [26] or charge-coupled device (CCD) [27], with the result that comparable limits of detection between continuum- and line-source GFAAS are now achieved throughout the entire wavelength region. Continuum-source absorption systems are, however, in the developmental stage and they require redesign of conventional GFAAS instrumentation and methodology, in addition to novel data collection and processing systems. Hence, while intriguing, this approach cannot readily be implemented at present.

A less complicated means of achieving simultaneous multielement analysis with the graphite furnace is to utilize a secondary source for excitation, such as a plasma formed within the graphite tube [28] or one which is spatially separated from it [29-31]. In this manner, the advantages in sensitivity, nearly 100% atomization efficiency and sample pretreatment inherent to the graphite furnace are retained. The graphite furnace serves to thermally desorb analyte from the graphite surface into atoms in the plasma, wherein efficient excitation of energy levels well in excess of 4 eV can be achieved. Several configurations have been developed which utilize glow discharges within graphite furnaces. Two function at reduced pressure and utilize the graphite tube either as the hollow cathode [22,28,32-34] or hollow anode [35-38] of a glow discharge. In 1989, an atmospheric pressure counterpart of these approaches was developed and termed Furnace Atomization Plasma Emission (Excitation) Spectrometry or FAPES [39,40]. In FAPES, an rf plasma is formed in helium or argon around a nominally 1-mm outside diameter (o.d.) graphite electrode, co-axially centred in a graphite tube. Aqueous samples may be introduced into the graphite furnace and subjected to the normal thermal pretreatment protocols of GFAAS to minimize matrix effects. The plasma is then ignited and the graphite furnace is then ramped to high temperature to vaporize the sample into the plasma, where it forms excited-state atoms. Such an approach could prove fruitful to enabling simultaneous multielement analysis with the graphite furnace because of increased analyte residence times at atmospheric pressure, coupled with throughput which is identical to GFAAS.

Organization of the thesis

This thesis has been divided into two sections. The first examines practical and fundamental aspects of a direct-current (dc) powered low-pressure glow discharge atomizer for cathodic sputtering of conductive solid samples. Chapter 1 provides a detailed examination of the response of atomic absorption and emission signals to alterations in the power, pressure and flow rate in such a source, with the aim of characterizing a stable regime for the processing of analytical measurements. Limitations in the design of the atomizer and in the response of glow discharge lines to self-absorption are highlighted. Chapter 2 focuses on the relationship between the widths of emission lines in hollow cathode lamp (primary) sources and those of absorption lines in the glow discharge atomizer. Currently, all atomic absorption spectrometers utilize the Walsh method of absorbance measurement [41], one of the assumptions of which is that the emission linewidth in the primary source is negligible in comparison to the absorption linewidth in the atomizer. Although this situation will certainly hold for atmospheric pressure flames and furnaces, in which a high degree of Doppler and Lorentz broadening occurs, the low operational thermal temperatures and pressures of glow discharge devices will nearly eliminate Lorentz broadening and substantially reduce Doppler broadening to the point that the absorption linewidth in the glow discharge may be of comparable magnitude to that in the hollow cathode lamp. This close conformity will have significant consequences for quantitative analysis by glow discharge atomic absorption spectrometry, in that deviations from linearity may be experienced earlier than for thermal sources such as flames and

furnaces. High-resolution Fourier transform spectrometry is used to obtain line profiles of emission lines at a number of lamp currents, as well as Doppler temperatures and absorption profiles in the glow discharge.

The second part of this thesis attempts to characterize Furnace Atomization Plasma Emission Spectrometry (FAPES) using two-dimensional imaging of the source with a charge-coupled device (CCD) camera. This is necessitated because of the inhomogeneity of the FAPES source. Chapter 3 deals with the response of plasma gas and background species to changes in tube material and centre electrode dc bias, as well as highlighting the role of the centre electrode as a site for secondary condensation and re-volatilization of analyte. Chapter 4 examines the effect of easily-ionized elements (EIEs) as interferents in analyte excitation, as well as the role of the dc bias of the centre electrode in changing plasma structure.

CHAPTER 1

CHARACTERIZATION OF A LABORATORY-CONSTRUCTED GLOW DISCHARGE ATOMIZER FOR DIRECT ANALYSIS OF SOLID SAMPLES

1.1 INTRODUCTION

A glow discharge is one of several types of gas discharges formed when two electrodes are immersed in a gas and sufficient potential is applied between them to cause the atoms and molecules of the gas to ionize, forming electrons and ions which results in the flow of current [3]. Although the majority of species are neutral, the conductive gas is termed a discharge or plasma. As a consequence of electric fields developed between the two electrodes, positively-charged species will be accelerated to the cathode (negative electrode), whereas negatively-charged species will be attracted to the anode (positive electrode). The breakdown potential required for the plasma to form is dependent upon the identity and density of the gas, the electrode material and interelectrode spacing and the extent of pre-existing ionization [3]. After the discharge is initiated, collisional processes within it produce more charged species, with the result that the discharge becomes "self-sustaining" provided that a suitable "maintenance" voltage, which is usually less than the breakdown voltage, is continually applied [3].

The evolution of a glow discharge can be considered by examining its current-voltage characteristics, as illustrated in Figure 1. The Townsend discharge regime (dark discharge) is characterized by low pressure operation (< 1 mtorr) and low current, implying few ionizing collisions as a consequence of which the production of electrons

Figure 1. Current-voltage relationships for various types of gas discharges. V_b is the breakdown voltage, V_n is the normal operating or maintenance voltage and V_d is the operating voltage for an arc discharge [3,42].

and ions is small. If the energy exchange between collisions is permitted to increase by use of a higher operating pressure, the current increases while the maintenance voltage of the discharge drops. This is the transition region between the Townsend and glow discharge regimes, sometimes termed the sub-normal regime [43]. As the voltage stabilizes, a luminous glow begins to form between the electrodes, characterizing the normal glow discharge regime. In this regime, the glow only partially covers the cathode, with the result that increases in current do not bring about increases in the current density, so no increase in voltage occurs [3]. When the current becomes sufficiently large to cause the glow to cover the entire cathode surface, further increase in current brings about an increase in current density and a corresponding increase in voltage. This is the "abnormal" glow discharge regime and it is this type of glow discharge that forms the basis for nearly all analytical atomic spectrometric applications of glow discharges. The final regime shown in Figure 1 is a dc arc, which is also widely used in analytical atomic spectroscopy. Dc arcs result when the current density increases and bombardment of the sample cathode by discharge gas ions becomes so intense that thermal vaporization of the cathode material occurs. Dc arcs are characterized by high operating currents (10-10,000 A) and high gas temperatures (up to 20,000 K) which result in the vaporization of large amounts of the sample (cathode) material [3].

1.1.1 Glow Discharges

A glow discharge possesses up to eight distinct regions depending on the pressure, the type of discharge gas used, the geometry of the containment vessel and the size, shape, separation and composition of the electrodes [43]. For the sake of simplicity, a parallel plate electrode system will be considered first. A representative diagram of a glow discharge in neon at 1 torr formed between two parallel plate electrodes is presented in Figure 2. In this configuration the discharge is composed of an Aston dark space, a cathode glow, a cathode dark space (sometimes also referred to as a Crookes or Hittorf dark space), a negative glow, a Faraday dark space, a positive column, an anode dark space and an anode glow. With the exception of the cathode dark space, a glow discharge can exist without all of these other regions [44]. It should be pointed out that dark spaces are not regions of zero emission intensity, but regions where the intensity of the emitted light is small in comparison to its surroundings. The emission intensity varies throughout each region of the discharge. In fact, the emission intensity of the anode dark space is slightly greater than that of the cathode glow, which only appears luminous because it is surrounded by two less luminous regions [44].

Because electrons are repelled from the vicinity of the cathode, a net positive space charge is built up in this region. As a result, the bulk of the voltage developed between the two electrodes is dropped across the narrow region near the cathode termed the cathode dark space [3]. This large potential gradient permits positive ions of the discharge gas to be accelerated towards the cathode surface, where they can impact with it producing

Figure 2. Different luminous regions in a parallel plate glow discharge formed in Ne at a pressure of 1 torr [43]. I is the emission intensity, V is the potential, V_c cathode fall potential, d_c is thickness of the cathode dark space, E_x is the electric field, n^+ and n^- are the positive and negative space-charge density, respectively, and j^- and j^+ are the positive and negative current density, respectively.

secondary electrons. It is the presence of these secondary electrons which produces the region of negative space charge that characterizes the Aston dark space [3]. At this point, the secondary electrons have not yet been accelerated by the cathode potential. Some of them may undergo exciting collisions with species from the discharge gas, producing the very weak emission which is characteristic of the cathode glow. Those electrons which do not undergo collisions in the cathode glow can then be accelerated, acquiring energies up to that of the cathode fall potential [3,45]. Because of the high energy of these electrons, they have a very low probability for undertaking exciting or ionizing collisions, with the result that a region of very low luminosity, the cathode dark space, results. As the majority of the discharge potential is (reasonably linearly) dropped across the cathode dark space, the thickness of the cathode dark space is an important consideration in glow discharge source construction. The thickness of the cathode dark space can be estimated as being three times the Debye length, λ_D , where

$$\lambda_D = (kT_e \epsilon_0 / n_e e^2)^{1/2} \quad (1.1)$$

In equation (1.1), k is the Boltzmann constant, T_e is the electron temperature, ϵ_0 is the permittivity of free space, n_e is the electron density and e is the charge on the electron. The potential developed across the cathode dark space (cathode fall) is termed the cathode fall potential.

The negative glow region begins where fast electrons from the cathode have lost a large fraction of their energy through elastic collisions with other particles [3]. In the negative glow, three groups of electrons exist [46]. Group I electrons are the fast or primary electrons, which consist of secondary electrons emitted from the cathode that have

gained kinetic energy through the cathode dark space, reaching energies of 20-25 eV and number densities of about 10^6 cm^{-3} (for an argon discharge at 5 - 15 torr [3]). Group II electrons are comprised of secondary electrons resulting from gas-phase ionization collisions. As a result of these inelastic collisions, Group II or slow electrons have energies in the approximate range of 2 - 10 eV and number densities from $10^7 - 10^8 \text{ cm}^{-3}$. Group III electrons are termed ultimate electrons, have number densities of $10^9 - 10^{11} \text{ cm}^{-3}$ and are comprised of Group I and Group II electrons that have undergone numerous elastic and inelastic collisions with particles in the plasma which have attenuated their energies to 0.05 - 0.6 eV [3]. Because of their high energy, fast (Group I) electrons are only capable of participating in ionizing collisions, whereas slow (Group II) electrons may interact with atomic or molecular species in the negative glow, producing excited-state or ionic species. The negative glow is essentially field-free as a consequence of the approximately equal numbers of (slow) electrons and positive ions comprising it. The voltage across the negative glow is fairly uniform, varying negligibly with large changes in the discharge voltage [47,48]. The negative glow is the most luminous region of the entire discharge and it is because of this and its collision-rich environment, that it is the region that is most widely used in analytical spectrometric applications.

Electrons that diffuse out of the negative glow have had their energies depleted through ionizing and exciting collisions such that they are only capable of producing weak emission with discharge gas species. This region of low emission intensity comprises the Faraday dark space. In the Faraday dark space the potential gradient increases slowly towards the anode such that electrons emerging from this region begin to be accelerated toward this electrode [3].

The energy gained by the electrons in the Faraday dark space allows them to again undergo excitation collisions, although at a decreased field strength, forming a region of luminous intensity which is the positive column. The positive column is perhaps the best understood region of the glow discharge, having been the subject of much early attention [43]. Of all the regions of the glow discharge, the positive column is the most strongly dependent upon the geometry of the glow discharge cell and will expand to fill the volume between the cathode and the anode [44].

In the area near the anode are the two remaining regions of the glow discharge: the anode dark space and the anode glow. The anode dark space arises as a result of the build-up of negative space charge near the anode [44]. This anode sheath permits electrons travelling from the positive column to the anode to be accelerated in the anode fall, eventually undergoing exciting collisions and producing an anode glow at the surface of this electrode [44].

1.1.2 Variation of Glow Discharge Structure with Changes in Operating Parameters

The complex glow discharge structure described above can be changed by alteration of source pressure, source geometry, electrode separation and the discharge voltage. For the parallel-plate glow discharge geometry of Figure 2, the negative glow and the dark spaces surrounding it shrink towards the cathode as pressure is increased. The negative glow shrinkage is related to the decreased mean free path of electrons, whereas the cathode dark space shrinkage is as result of the increased depth of positive ion

penetration into the positive space charge region near the cathode due to the corresponding decrease in electron temperature [43,49,50]. The positive column, however, extends laterally to fill the remaining space, although it contracts radially with increasing pressure [44]. As voltage is increased, the length of the negative glow expands as a result of the enhanced electron energy in the discharge [44] and the cathode dark space thickness (which is inversely proportional to the cathode fall voltage) decreases. A greater proportion of high-energy ions is then able to reach the cathode [43,51]. By analogy to the effect of a decrease in pressure, the positive column should contract towards the cathode with increased voltage as the space for its formation is reduced. As the electrode spacing is increased, the voltage required to maintain the glow discharge increases slightly, the positive column expands to fill the new volume and little change occurs for the dimensions of the other regions in the glow discharge [44]. The dimensions of the positive column are also influenced by the frequency of the discharge; high-frequency discharges cause a radial contraction of the positive column [43]. As the electrode spacing decreases, the maintenance voltage decreases and the positive column shrinks, followed by the Faraday dark space, until both eventually disappear when the interelectrode separation is only a few times greater than the cathode dark space thickness [51]. If the distance between the electrodes is less than twice the dark space thickness, the dark space is distorted and the discharge extinguishes [51]. The cathode dark space and the negative glow are, however, unaffected by a decrease in electrode separation. When this separation is brought to its extreme minimum, an "obstructed" glow discharge results in which only the cathode dark

space and the negative glow form. The obstructed glow discharge is the type most frequently employed in analytical glow discharge spectrometry.

1.1.3 Cathodic sputtering

The process by which atoms of the sample (cathode) are ejected into the glow discharge as the result of bombardment by ions of the discharge is termed “cathodic sputtering”. First observed in 1852 [52], cathodic sputtering was initially considered a nuisance because it eroded electrodes and redeposited sputtered material around the walls of the chamber, impeding studies of the luminous zones of the glow discharge. The realization that cathodic sputtering could serve as an efficient and uniform means of solid sample ablation without some of the instabilities and matrix effects inherent to thermal ablation methods, however, provided the impetus for many investigations into the nature of the cathodic sputtering process.

Cathodic sputtering in a glow discharge occurs because the high cathode fall potential in the cathode dark space provides a pathway for positive ions from the negative glow to be accelerated to the cathode surface, provided their random motion brings them near the negative glow/cathode dark space boundary. As the discharge gas ion impacts on the cathode surface it penetrates the solid, transferring its energy to the production of secondary electrons and imparting its energy and momentum to the atoms comprising the cathode lattice *via* a number of inelastic and elastic collisions. The incident discharge gas ion may also be backscattered from a surface atom into the negative glow, but this event

is rare, having an estimated probability of only 0.3% [53]. Each discharge ion that collides with the cathode surface produces a collision cascade within the lattice lasting for approximately one picosecond [54], propagating randomly from the initial impact site. Surface atoms that acquire velocity vectors near the surface normal can be ejected from the cathode, provided the energy they receive exceeds the surface binding energy [3,55]. This process is known as physical sputtering and is depicted in Figure 3.

The actual energy with which a discharge ion bombards the cathode surface will be dependent upon the number of collisions it experiences between the point of its formation at the negative glow/cathode dark space interface and the cathode surface. Symmetric charge-exchange, wherein an energetic (fast) positively-charged discharge gas ion collides with a slow discharge gas atom to yield a slow (thermal) ion and a fast atom, is responsible for attenuating the energy of discharge gas ions to thermal levels [56,57], as illustrated below [3]:

The resulting thermal ion can then be accelerated by the remaining fall potential between the point of symmetric charge exchange and the cathode [3]. The degree to which these collisions occur will be dependant upon the discharge pressure and voltage and the thickness of the cathode dark space. Positively charged particles may lose and regain their charge many times on passage through a gas, thus allowing a small number of ions to bombard the surface with the full energy gained in the cathode fall. The preponderance

Figure 3. Idealized representation of cathodic sputtering and atomization, excitation and ionization processes in the glow discharge [3-5,53].

of impacting discharge ions will have lost roughly 80% of their initial energy as a consequence of collisions [58].

Although atoms, molecules [53,59-64], dimers [65-67], atomic clusters [55,68,69], positive and negative ions, secondary electrons and photons may all be ejected from the cathode surface, the majority of material ablated from the cathode exists in the form of ground-state neutral atoms. Any ejected positive ions, of which about 1% of the sputtered material is comprised [70], are immediately returned to the surface of the negatively-charged cathode, whereas electrons will be accelerated away. More significantly, owing to the atomic mean free paths, which are less than 0.1 mm at typical glow discharge operating pressures of 0.1-20 torr, sputtered atoms will undergo numerous elastic collisions with discharge gas species, thus rapidly losing their momentum. In this manner, sputtered atoms return to the cathode surface. Indeed, it is estimated that up to 95 % of sputtered atoms are redeposited at a pressure of 1.5 torr in argon [71]. Clearly, this situation poses a substantial limitation for analytical applications of cathodic sputtering, particularly in regard to the determination of analytes at trace or ultra-trace levels. As will be considered later, however, redeposition is most severe in "static" glow discharge sputtering cells which employ no flow of discharge gas to enhance the otherwise diffusion-controlled movement of sputtered atoms.

The sputtering yield is typically defined as the number of atoms sputtered from the sample surface per incident ion. A general equation for deriving sputtering yield (S) has been proposed by Sigmund [72]:

$$S = \frac{3\pi^2\alpha}{4} \left[\frac{4 M_1 M_2}{(M_1 + M_2)^2} \right] \frac{E}{U_o} \quad (1.3)$$

where M_1 is the mass of the discharge ion, M_2 is the mass of the sputtered atom, E is the energy of the bombarding ion, U_o is the surface binding energy and α is a function of the relative masses and the angle of incidence of the incoming ion. This equation is impractical to use experimentally in cathodic sputtering since the energies and angles with which the incident ions hit the cathode vary and measurement of these terms is problematic. Another equation which is practical to use expresses the sputtering yield in terms of sputtered atoms per incident ion [73]:

$$S = 9.6 \times 10^6 \left(\frac{W}{Mi^*t} \right) \quad (1.4)$$

where W is the weight lost from the cathode in grams, M is the atomic mass of the sputtered species in grams, i^* is the bombarding ion current in amperes and t is the sputtering time in seconds. The bombarding ion current can be obtained in relation to the total discharge current i and the average number of secondary electrons released by one ion, γ_i (which approximates to 0.1 for glow discharges in Ar, the most commonly used sputtering gas [3]), as follows:

$$i^* = \frac{i}{1 + \gamma_i} \quad (1.5)$$

The only limitation of Equation 1.4 relative to Equation 1.3 is that the sputtering yield term now includes atoms which have been redeposited onto the cathode surface, since it is based on weight loss measurements made before and after sputtering. Most elements exhibit close conformity (within one order of magnitude) in sputtering yields [56], in contrast to their more widely divergent evaporation rates. For example, the evaporation rates of aluminum and tungsten differ by more than nine orders of magnitude at 2000 °C, whereas their respective sputtering rates differ by only a factor of two [20]. This would suggest that cathodic sputtering in a glow discharge has the potential to provide a significantly more uniform sampling of surfaces than techniques relying purely on thermal evaporation.

Despite this general uniformity of sputtering, there are many characteristics that cause deviations from the “ideal” behaviour discussed above. One of the most significant of these occurs in the sputtering of alloys. The various components of an alloy will sputter preferentially according to their respective sputtering yields, leaving the cathode depleted in elements with high sputtering yields and enriched in elements having low sputtering yields. Once a layer of the more easily sputtered elements is removed, the sputtered flux from the cathode will be enriched in elements with low-sputter yields, until the layer(s) containing them are removed from the cathode surface and a “new” layer of high-sputtering yield elements is exposed [3,74,75]. Because of the rapidity of this process and the law of conservation of mass, however, a steady state is established after a few monolayers are removed. At steady state, the relative surface composition of a two-component system (A and B) can be calculated from:

$$\frac{C_A}{C_B} = \left(\frac{P_B C_{i,A}}{P_A C_{i,B}} \right) \quad (1.6)$$

where C_i is the bulk composition of the atom and P is its ejection probability. Using Auger spectroscopy of a thin film placed in the negative glow region, Fang and Marcus [21] found that the Cu:Zn peak height ratios of deposits on the film were nearly identical to those of the bulk sample. These data suggest that preferential and differential sputtering notwithstanding, glow discharge sputtering occurs in a stoichiometric fashion such that the composition of the plasma is reflective of the bulk sample [3]. Differential sputtering may be more of a concern for depth profiling applications of cathodic sputtering, rather than bulk sampling, particularly if fine depth resolution is desired.

The roughness of the sample surface, its form and temperature, the angle of incidence and energy of the bombarding ion and the presence of impurities in the discharge gas also influence the sputtering yield. It is general practice to grind and polish the cathode surface prior to introducing it into the glow discharge in order to present a more uniform surface. Pre-sputtering, or removal of the first few layers of the cathode surface, provides the most uniform surface and this procedure is usually carried out prior to the analytical measurement. Such preparations are necessary as irregularities on the cathode surface can make it more difficult for an atom to acquire a velocity vector normal to the cathode surface and thus be sputter ejected from it. The conductivity of the sample is also of paramount importance for dc glow discharge devices because the sample acts as the negative electrode of the glow discharge and must conduct electricity (electrons) [3]. Difficulties arise with metals or alloys which are prone to oxide formation, since not only

are such oxide layers strongly-bound and resistant to sputtering, but also because they exhibit decreased electrical conductivity. Non-conducting samples have traditionally been dealt with in glow discharge analysis by grinding and mixing the sample together with a metal powder or graphite to produce an electrically-conductive composite pellet [76,77]. As this procedure dilutes the sample and has the potential for adding impurities, many researchers have turned their attention to radio-frequency (rf) sputtering as a means of sputtering non-conductors. Application of high rf potentials to the nonconducting sample induces a capacitor-like response, allowing the sample to acquire the applied potential. Provided the sample (electrode) area is smaller than that of the counter electrode (discharge cell housing), it can acquire a negative dc self-bias voltage, permitting the "sample electrode" to function as a cathode for a longer period of time than the counter electrode, thus sustaining the discharge [3].

Since some of the kinetic energy of the bombarding ion is converted to heat at the cathode surface, the cathode temperature can rise, particularly during prolonged sputtering. If the temperature of the cathode surface approaches within 250°C of the melting points of the analyte metals contained within it, there will be an initial apparent increase in sputtering yield as vaporization begins to take place [56,78]. Long periods of cathode heating can anneal exposed atoms to areas of greater binding energy, making them more difficult to sputter. For these reasons, most glow discharge systems employ cooling systems which minimize the temperature rise of the cathode.

The sputtering yield increases with the energy of the bombarding ion (which is proportional to the cathode fall potential and mass) and the electrical current [50]. The

angle of incidence also influences sputtering yield since it is more likely that ions impinging the cathode surface nearly parallel to it will simply reflect off. Optimum angle of incidences tend to be 70-80° to normal, with the exact angle depending on a number of conditions [79]. Because of the nonuniform electric field near the cathode surface, ions will impact the cathode surface at various angles. Finally, molecular impurities in the discharge gas can decrease the sputtering yield, most likely by attenuating the energy of electrons and ions in the plasma *via* collisions. In particular, water vapour has a pronounced effect on lowering the sputtering yields in glow discharges [80].

1.1.4 Analyte Atomization, Excitation and Ionization

Atoms sputtered from the cathode surface that survive transit into the negative glow can undergo numerous collisions with electrons, ions and metastable atoms. The collisions most likely to take place in a negative glow region of a glow discharge are listed in Table 1. A primary consideration of the mechanism prevalent in such a source, in addition to its geometry and experimental conditions, must be the degree of conformity or “resonance” between energy levels of the analyte and that of the colliding species [3]. Although a significant degree of atomic excitation occurs through electron impact, Penning collisions are also important in producing excited-state atoms and ions [51,81]. Penning collisions are those in which collisions between metastable fill gas atoms and sputtered neutrals result in a transfer of internal energy from the metastable to the neutral atom, producing an excited-state atom, ion or excited-state ion. Indeed, Penning ionization is

Table 1. Typical excitation and ionization mechanisms in a glow discharge [3].

I. Primary excitation and ionization processes.

II. Secondary Processes

A. Charge transfer

III. Primary de-excitation and ionization processes

M^0 represents a sputtered neutral atom, A_m^* represents a metastable discharge gas atom and

X represents any gas-phase atom.

believed to be the dominant mechanism of analyte ionization in the glow discharge, accounting for 50-95% of the total analyte ionization [82]. Asymmetric charge (energy) exchange is also an important means of ionization or excitation in the glow discharge [83,84], provided that the energies between the collision partners are closely matched, usually within a few tenths of an electron volt [85]. It should be remembered, however, that only 1% of total flux of sputtered atoms will be excited in the negative glow and that only an additional 1% will be ionized. The preponderance of sputtered material will exist as ground-state neutral atoms, making atomic absorption a sensitive means of probing the negative glow. The development of sputtering cells designed to maximize the sensitivity of atomic absorption in glow discharges will be considered next.

1.1.5 Glow Discharge Atomizers in Atomic Absorption Spectrometry

The application of glow discharges as atomization sources for atomic absorption spectrometry was first proposed by Russell and Walsh in 1959 [86]. Subsequently, Gatehouse and Walsh [87] applied a sputtering cell to atomic absorption analysis, in which sample formed the hollow cathode. Hollow cathodes were also used as substrates on which analyte elements were dried prior to atomic absorption analysis [88]. Flat electrodes on which samples were dried have been used as replaceable cathodes in a sputtering cell with a flowing gas stream [89]. A common feature to nearly all early applications of glow discharge cells was the absence of a flowing gas stream. As noted before, in such "static" glow discharge systems, redeposition of sputtered atoms can be

severe [71] and ultimately will limit the sensitivity attainable. Gough *et al.* [90] first described a sputtering cell employing directed gas flow in which samples could be introduced as flat cathodes for atomic fluorescence measurements and later redesigned this cell for atomic absorption measurements [91]. In the latter design, a gas flow entered near the surface of the flat sample cathode and flowed into the cell body, thus effecting improved transport of sputtered neutrals into the analysis volume and reducing sample redeposition [91].

In 1986, this concept was expanded upon by Analyte Corporation (Medford, Oregon, USA) in the design of the first commercial glow discharge atomizer specifically geared to atomic absorption spectrometry, known as the Atomsources™ [92]. The Atomsources is unique among the devices already discussed in this chapter in that it employs a Grimm-type discharge [93] (*i.e.*, obstructed geometry) and has six high-velocity gas “jets” etched into the anode through which discharge gas can impinge upon the cathode surface. The obstructed geometry brings the anode and cathode in close proximity to one another such that only a cathode dark space and a negative glow form, thus simplifying the analysis volume. The gas jet flow is such that it impinges upon the cathode surface and efficiently sweeps sputtered atoms out into the body of the atomizer. The latter is of a “T”-shaped configuration with pumping ports at either side, thus extending the absorption path length and enhancing sensitivity. Samples are introduced into the discharge as flat cathodes, which simplifies sample preparation and increases sample throughput. A diagram of a modified Atomsources cell that was used in Chapters 1 and 2 of this thesis is presented in Figure 4.

Figure 4. Schematic diagram of the modified Atomsources atomizer used. The components are as follows: (a) is the ceramic arrestor; (b) is the main body of the atomizer; (c) is the cathode plate; (i) is insulating material; (j) is the anode with six jets for gas flow; (s) is the sample; (v) is the vacuum system and (w) is the water cooling channel [92,98,102].

Since its introduction, the Atomsources have been applied to the analysis of steel alloys [94] and has served as the basis for fundamental and applied research in a number of laboratories. The groups that have amassed perhaps the greatest amount of theoretical and practical expertise on the Atomsources are those of Chakrabarti and co-workers [6-11,14], Piepmeier and co-workers [12,95-98], Blades and co-workers [16,17,99-101] and Marcus and co-workers [76,77,102]. Although the range of application in the above laboratories was diverse, several general limitations of the Atomsources soon became apparent. Foremost of these was the fact that the Atomsources regulate internal cell pressure by changing the flow rate of the discharge gas, making modification of the source to permit independent control of cell pressure and discharge gas flow rate essential [10,11,12,16]. An additional limitation of the Atomsources lay in the power supply provided with it, which permits regulation of discharge current only. For a constant pressure, an increase in discharge current will bring about an increase in discharge voltage as a consequence of increased current density at the cathode surface [107]. As pressure is increased for a given input current, the voltage will decrease as a consequence of more efficient collisional processes that occur at elevated pressure. This results in lower initial secondary electron energies required to maintain the discharge [51]. At higher pressures, electrons lose their energies more efficiently through collisions [3,43]. The inverse proportionality between voltage and pressure, coupled with the interrelationships existing between current, voltage and power [51], as well as the added complexity of the gas jets which may produce local excesses of pressure in the cell, suggest that operation of Atomsources-type discharges by regulation of either current or voltage have the potential

to create undue variation in sputtering characteristics. Since power is the product of voltage and current, operation of Atomsources-type devices by power regulation should provide an added degree of control to the sputtering over a wider variety of pressure and flow rate regimes than current or voltage regulation. Applied power fixes both current and voltage (although each will “float” to its respective value for a given pressure and flow rate). Even if constant power regulation is employed, the interrelationships between discharge parameters noted above will still produce complex dependencies amongst them and the resulting absorption and emission signals *via* analyte sputtering [11,12,16,17,99].

In view of the limitations in the commercial design of the Atomsources, independently-constructed modifications to this cell design were made by Chakrabarti and co-workers [10,11] and Blades and co-workers [16,17]. The geometry of the sputtering cell used in this study is identical to the Atomsources. A mass flow controller was mounted onto the gas inlet line of the source to monitor and control the flow rate of the gas entering the gas jets. A regulating valve and Pirani gauge were mounted on the outlet line to the vacuum pump to control and monitor the pressure, respectively [11]. The cell was connected to a power supply capable of power, current, or voltage regulation up to 1000 W, 1 A or 1000 V [11]. Further details will be provided in the Experimental section of this chapter.

In an initial study with this new atomizer, Hutton *et al.* [11] found that the discharge voltage decreased as gas flow was increased, in accordance with the results of Kim and Piepmeier [12]. Banks and Blades [17] concluded that the gas jets serve to initiate or exacerbate self-absorption of certain iron, copper, nickel and chromium

emission lines. Our previous work showed that the emission intensity of the Cu I 324.75 nm resonance line reached a maximum at a specific flow rate and decreased at higher flow rates [11]. This was attributed to a decrease in the discharge voltage with increasing flow rate, which reduced the energy of fast electrons, causing electron-impact excitation of ground-state copper atoms to become less efficient [11]. This explanation, however, did not take into account possible self-absorption broadening of the copper resonance line.

Using a jet-assisted glow discharge atomizer with independent control of pressure and flow rate, Banks and Blades [17] found that an increase in power brought about a comprehensive increase in the intensities of emission lines in the absence of gas flow. With the application of flow through the gas jets, however, they observed enhanced emission intensities for certain lines and decreased emission intensities for others [17]. They calculated absorption coefficients for the observed emission lines and found that lines which decreased in intensity with increasing jet flow rate possessed large absorption coefficients, while those that increased in intensity had relatively small absorption coefficients [17]. By using a high-resolution échelle monochromator with a linear photodiode array detector, they were able to obtain point-by-point maps of the intensity distribution around the Cu I 324.75 nm resonance line. Analysis of this roughly approximated "line profile" revealed that the Cu I 324.75 nm resonance line decreased in intensity and was broadened at the wings when flow through the gas jets was applied [17]. This led the authors to propose that resonance lines and atomic lines with lowest-lying energy levels close to the ground state were being self-absorbed as a result of the gas flow through the jets [17]. Self-absorption and reversal of the Ca I 422.67 nm and Cr I 425.4

nm resonance lines in a Grimm glow discharge lamp was reported by West and Human [104]. De Jong and Piepmeier [105] observed self-reversal of the Cu I 324.75 nm line in pulsed hollow cathode lamps.

The purpose of this chapter is to characterize the performance of this atomizer for the direct determination of solid samples and to further understanding of the dependence of absorbance and emission signals on the power, pressure and flow rate. Nickel was used as the test element for the parametric evaluation of the atomizer and its absorbance was measured by sputtering two different cathode materials. The potential contribution of self-absorption to a copper resonance line was assessed by measuring the emission intensity of this line and a copper ion line as a function of pressure, flow rate and power. High-resolution measurements of the shape of an iron resonance emission line were also made to assess self-absorption effects.

1.2 EXPERIMENTAL

1.2.1 Reagents and Instrumentation

The gas control system used in this chapter is identical to one used in an earlier investigation [11] and a block diagram of it is presented in Figure 5. Argon (99.997% pure), which had been passed through a moisture trap (Model No. MT120-4, Chromatographic Specialties) and a particulate filter (Matheson Gas Products), was used as the discharge gas. The flow rate was controlled on the gas inlet to the atomizer with a Nupro fine-regulating needle valve and measured using the flow rate transducer of a

Figure 5. Block diagram of the glow discharge atomic absorption spectrometric system permitting independent control of the pressure and flow rate of the gas in the atomizer. A: Digital recording oscilloscope (replaced by a PDP-11/73 minicomputer for Fourier transform spectroscopy); B: monochromator and detection system (replaced by the Bomem DA3.002 Fourier transform spectrometer); C: atomizer (1 anode, 2 cathode); D: hollow cathode lamp; E: gas solenoid; F: Pirani gauge; G: flow transducer; H: ball valve for coarse control of gas pressure; I: regulating valve for fine control of gas pressure; J: fine needle valve for control of gas flow rate; K: foreline trap; L: two-stage vacuum pump; M: power supply; N: argon gas tank and regulator; O: particulate filter and moisture trap [11].

mass flow controller (Sierra Instruments, model No. 740-05-2). The pressure in the atomizer was adjusted on the outlet line to the vacuum pump (Model 5 Edwards High Vacuum) with a Whitey ball valve for coarse control and a Whitey regulating valve for fine control. A Pirani gauge (Model No. 275 Granville-Phillips Convectron Gauge), mounted on the outlet line, was used for pressure measurement. Cathodes were polished to a smooth surface with 400-grit emery paper on an electric sander, cleaned with ethanol and air-dried prior to use. They were clamped to the water-cooled cathode plate of the atomizer, which was subsequently evacuated to approximately 300 mtorr. The needle valve on the gas inlet was adjusted to the desired flow rate and the valves on the vacuum line were adjusted to provide the desired pressure. The discharge was initiated at the desired power by triggering the power supply (Model MDX1K, Advanced Energy Industries, Ft. Collins, CO, USA) and plots of signal intensity as a function of time were obtained using a lock-in amplifier and dual-channel digital oscilloscope (Model 201, Nicolet Instrument Corp.). Atomic absorption and emission signals were then studied as functions of power, flow rate and pressure by (i) varying flow rate and power at a constant pressure of 15 torr; (ii) varying flow rate and pressure at a constant power of 100 W; and (iii) varying power and pressure at a constant flow rate of 0.5 (standard) L min⁻¹.

1.2.2 Measurement of atomic absorption and emission

The Ni I 232.00 nm, Cu I 324.75 nm and Fe I 248.33 nm resonance lines and the Cu II 224.70 nm line [106] were selected for study. The absorbance of nickel at 232.00

nm was obtained by sputtering blocks of bulk brass and National Institute of Standards and Technology (NIST) electrolytic iron standard reference material (SRM) No. 1265a, (containing nickel at 0.041 wt. %). A Westinghouse hollow cathode lamp was used at a current of 9 mA and a modulation frequency of 1 kHz. A spectral bandpass of 0.33 nm was employed. Knowledge of the actual nickel concentration of the bulk brass sample was not critical for this work since it was used solely to determine the effect of changes in the experimental parameters on the measured absorbance.

Atomic emission of copper was measured by sputtering blocks of 99%-pure copper. Both a neutral atom line (Cu I 324.75 nm) and an ion line (Cu II 224.70 nm) were used. The spectral bandpass was 0.082 nm. For the ion line, pressure and flow rate were varied at a constant power of 150 W, instead of 100 W, to obtain suitably large emission signals.

1.3.3 Emission Line Profile Measurements

High-resolution measurements of emission line profiles were made with a Bomem Model DA3.002 Fourier transform spectrometer equipped with a Hamamatsu R166 solar-blind photomultiplier. The Cu I 324.75 nm line profile was measured by sputtering a 99%-pure copper block at a constant applied power of 30 W and pressure of 10 torr while the flow rate was varied from 0.1 to 1.0 L min⁻¹. A bulk steel cathode was sputtered at an applied power of 50 W, flow rate of 0.5 L min⁻¹ and pressure of 10 torr for the measurement of the Fe I 248.33 nm emission line profile. Boxcar apodization was used for minimum distortion of spectral features. For the Cu I 324.75 nm line, the resolution

was 0.05 cm^{-1} (*i.e.*, 0.53 pm at 324.75 nm); for the Fe I 248.33 nm line, the resolution was 0.10 cm^{-1} (*i.e.*, 0.62 pm at 248.33 nm). Fifteen scans were co-added for total scan time of approximately fifteen minutes for both Cu and Fe lines.

1.3 RESULTS AND DISCUSSION

1.3.1 Atomic Absorption Studies

Figures 6 to 8 show the pressure, flow rate and power dependence of the absorbance by nickel sputtered from the electrolytic iron and bulk brass cathodes. Figure 6 illustrates the effects of varying flow rate and power at a constant pressure of 15 torr. For the electrolytic iron sample [Fig. 6 (a)], the nickel absorbance reached a maximum at about 0.5 L min^{-1} as the flow rate was increased and then remained essentially constant up to a flow rate of 1.0 L min^{-1} . The dependence of the nickel absorbance signal on power and flow rate for the brass sample [Fig. 6 (b)] is similar to that obtained for the sample of electrolytic iron. The absorbance reached a maximum at a flow rate of approximately 0.5 L min^{-1} and then decreased gradually at flow rates in excess of about 1.0 L min^{-1} . The decrease in absorbance at high flow rates is understandable since, at a constant pressure, flow rates in excess of those required to minimize redeposition of sputtered atoms onto the cathode or diffusion to the atomizer walls reduce the number of atoms in the analysis volume. The initial increase in nickel absorbance with increasing gas flow rate is likely a consequence of increases in both sputtering efficiency (defined as the fraction of the total number of analyte atoms that are sputtered from the cathode surface and are not

(a)

(b)

Figure 6. Absorbance response surface for nickel sputtered from: (a) NIST Standard Reference Material No. 1265a (electrolytic iron); and (b) bulk brass, as flow rate and power were varied at a constant pressure of 15 torr.

(a)

(b)

Figure 7. Absorbance response surface for nickel sputtered from: (a) NIST Standard Reference Material No. 1265a (electrolytic iron); and (b) bulk brass, as flow rate and pressure were varied at a constant power of 100 W.

(a)

(b)

Figure 8. Absorbance response surface for nickel sputtered from: (a) NIST Standard Reference Material No. 1265a (electrolytic iron); and (b) bulk brass, as pressure and power were varied at a constant flow rate of 0.5 L min^{-1} .

redeposited) and transport efficiency (defined as the fraction of the total number of analyte atoms sputtered from the cathode surface that reach the analysis volume). A previous study with this atomizer concluded that the maximum transport efficiency for sputtered atoms was attained at a flow rate of 0.5 L min^{-1} [11]. Thus, the fact that the absorbance by nickel remained essentially constant as flow rate was increased from 0.5 to 1.0 L min^{-1} in the present work again reflects an increase in the sputtering efficiency, which offsets the dilution in the number density of analyte atoms at flow rates up to 1.0 L min^{-1} . For both the iron and brass samples, absorbance increased with increasing power. This is in agreement with other investigations [17,107] which have established a positive correlation between sputtering rate and discharge power.

Figure 7 illustrated the effects of varying pressure and flow rate at a constant power of 100 W . The absorbance of nickel sputtered from both iron and brass increased with increasing flow rate until approximately $0.5\text{-}0.6 \text{ L min}^{-1}$. High flow rates could not be achieved at low pressures due to limitations in the capacity of the vacuum pump associated with the apparatus. For both cathode materials there was a slight decrease in the absorbance as the pressure was increased, presumably due to increased redeposition of sputtered atoms.

Figure 8 shows the effects of altering pressure and power at a constant flow rate of 0.5 L min^{-1} . In general, absorbance was found to increase with increasing power and to decrease with increasing gas pressure for both cathode materials. Figures 6-8 show the following trends for the dependence of the absorbance on power and pressure. An increase in power at constant pressure and flow rate brings about an increase in absorbance, most

likely because of an increase in the sputtering rate of the cathode surface [16,17]. An increase in pressure at constant power and flow rate brings about a small decrease in the absorbance, presumably because of increased redeposition of sputtered atoms. A change in the flow rate of argon at constant power and pressure has the most pronounced effect on the absorbance signal. In all cases, a minimum value of about 0.5 L min⁻¹ was required before the absorbance signal attained its maximum value. The absorbance then remained essentially constant as the flow rate was increased to 1.0 Lmin⁻¹. The dependence of nickel absorbance on pressure, flow rate and power was similar for the brass and iron cathodes.

1.3.2 Atomic Emission Studies

In an earlier study with this atomizer [11], the emission intensity of the Cu I 324.75 nm line (resulting from sputtering a bulk copper sample at constant power and pressure) was found to reach a maximum at a flow rate of about 0.5 L min⁻¹ and to decrease with further increase in the flow rate. This decrease was ascribed to a less efficient electron-impact excitation mechanism of ground-state copper atoms at high flow rates [11] and did not take into account self-absorption. This study attempts to highlight the effects of self-absorption by comparing the effects of pressure, flow rate and power on the emission intensity of the Cu I 324.75 nm resonance line to those of the Cu II 224.70 nm line. These results are presented in Figures 9-11. Use of an ion line will not guarantee freedom from self-absorption if the lower energy levels are metastable states.

Figure 9. Emission intensity response surface for: (a) the Cu I 324.75 nm resonance line; and (b) the Cu II 224.70 nm line, as flow rate and power were varied at a constant pressure of 15 torr.

Figure 10. Emission intensity response surface for copper as flow rate and pressure were varied at a constant power of: (a) 100 W for the Cu I 324.75 nm resonance line; and (b) 150 W for the Cu II 224.70 nm line.

Figure 11. Emission intensity response surface for: (a) the Cu I 324.75 nm resonance line; and (b) the Cu II 224.70 nm line, as pressure and power were varied at a constant flow rate of 0.5 L min^{-1} .

Fortunately, this is not the case for the Cu II 224.70 nm line. Additionally, several studies [83,108] have indicated that the Cu II 224.70 nm line is ionized and excited by a charge exchange mechanism with Ar^+ rather than by electron impact. Nevertheless, it is reasonable to assume that all excitation mechanisms in the plasma are ultimately controlled by electrons [22,109]. A comparison of line intensities between the Cu I 324.75 nm line and the Cu II 224.70 nm line is thus not without merit.

Figure 9 illustrates the effects of changing the flow rate and power at a constant pressure of 15 torr. At any given flow rate the intensities of both copper lines increased with increasing power, as a consequence of an increase in the sputtering rate [16,17,107]. At a given power, the emission intensity of the Cu I 324.75 nm resonance line reached a maximum at about 0.5 L min^{-1} and then decreased [Fig. 9 (a)], in agreement with previous results [11]. The Cu II 224.70 nm line emission intensity, on the other hand, continued to increase until a flow rate of 0.9 L min^{-1} was attained, after which the intensity decreased [Fig. 9 (b)]. This behaviour is in general agreement with the results of Banks and Blades [16] who observed that the emission intensity for this ion line increased with flow rates increasing beyond 0.05 L min^{-1} . They did, however, observe an initial decrease in the emission intensity of the copper ion line as flow rate was increased to 0.05 L min^{-1} [16]. A corresponding decrease in the emission intensity of the ion line was likely not observed in the present study because the lowest flow rate used was 0.1 L min^{-1} . Previous work with this atomizer [11] revealed that the absorbance of the Cu I 324.75 nm line, obtained by sputtering the NIST SRM No. 1263a (steel), reached a maximum at a flow rate of about 0.5 L min^{-1} and remained constant up to 1.0 L min^{-1} . This established the presence

of a large ground-state atomic population in the discharge between flow rates of 0.5 and 1.0 L min⁻¹, which is a favourable condition for self-absorption. The observation that emission from the copper resonance line decreased in intensity while the ion line intensity increased is a strong indication that self-absorption of the copper resonance line occurs.

Figure 10 illustrates the effects of varying the flow rate and pressure at constant power. The emission intensities of both the Cu I 324.75 nm resonance line and the Cu II 224.70 nm line decreased with increasing pressure at a given flow rate. This is likely a consequence of decreased redeposition of sputtered atoms at low pressure [107,110]. However, the intensities of the two lines again exhibited different characteristics as flow rate was increased. The intensity of the resonance line reached a maximum at a flow rate of about 0.5 L min⁻¹ and then gradually decreased [Fig. 10 (a)], whereas that of the ion line increased with increasing flow rate [Fig. 10 (b)] until high flow rates were reached. This characteristic of the emission intensities of both lines with increasing flow rate closely parallels that shown in Fig. 9, once again suggesting self-absorption of the copper resonance line.

Figure 11 illustrates the effects of varying pressure and power at a constant flow rate of 0.5 L min⁻¹. The intensities of both the resonance line and the ion line decreased with increasing pressure at a given power and increased with increasing power at a given pressure.

In summary, the emission intensity of both copper lines increased with increasing power as the result of an increase in the sample sputtering rate. An increase in argon flow through the gas jets has a more pronounced effect on emission intensities than on

absorbance signals because flow rate increases the width of the negative glow and the amount of material sputtered, both of which can contribute to self-absorption. An increase in pressure brings about a decrease in the intensity of both lines, likely as a consequence of increased redeposition.

1.3.3 High-Resolution Line Profile Measurements

Since the decrease in the intensity of the Cu I 324.75 nm resonance line with increasing flow rate (at a constant power and pressure) has been attributed to self-absorption [17], it was decided to obtain the profile of this line by Fourier transform spectrometry. Self-reversal of the Cu I 324.75 nm line is clearly evident from the data presented in Figure 12. In the absence of self-absorption, hyperfine splitting would cause the Cu I 324.75 nm line profile to appear as a doublet of intensity ratio 3:5 [111]. The observed quartet structure is due to self-reversal of the two groups of hyperfine components. Self-reversal of this line has been reported by Thorne for a Grimm glow discharge lamp [111,112] and a similar self-reversed profile was obtained by Larkins for a pulsed copper hollow cathode lamp operated at high current [113]. The Cu I 324.75 nm line was found to be self-reversed at all flow rates investigated in this study. As the flow rate was increased to about 0.5 L min⁻¹ at a constant power and pressure, the intensity of the self-reversed line initially increased and then decreased at higher flow rates. This provides additional information for the conclusion that 0.5 L min⁻¹ represents a flow rate at which the transport efficiency of sputtered atoms into the analysis volume is maximized.

Figure 12. Emission profile of the Cu I 324.75 nm resonance line obtained by Fourier transform spectrometry. The power applied was 30 W, the pressure was 10 torr and the flow rate was 0.5 L min⁻¹.

Figure 13. Emission profile of the Fe I 248.33 nm resonance line obtained by Fourier transform spectrometry. The power applied was 50 W, the pressure was 10 torr and the flow rate was 0.5 L min⁻¹.

To obtain additional information on the shapes of resonance emission lines in the glow discharge atomizer, the profile of the Fe I 248.33 nm line was obtained from sputtering a bulk steel sample. This line profile is given in Figure 13. The dots are experimental data points. The solid line is a least-squares fit of the data obtained by fitting Voigt profiles. Although the fit to the data is not very satisfactory owing to the small number of data points, it is clearly evident that the iron resonance line is also self-reversed. This line profile is very similar to that obtained by Larkins [113] for a pulsed iron hollow cathode lamp at high current. Self-reversal of the iron line also occurs over the entire range of flow rates, but maximal emission response is again attained at a flow rate of 0.5 L min^{-1} , once again indicative of transport efficiency being optimized in this flow rate region.

1.4 CONCLUSIONS

Previous work with this atomizer revealed that the atomic absorbance and, therefore, the ground-state population of copper, chromium and nickel, was at a maximum and steady-state in the flow rate range from 0.5 to 1.0 L min^{-1} [11]. It is not unreasonable to assume that a similar situation exists for iron, resulting in the self-reversal of the iron resonance line. The results presented in this study suggest that self-absorption of resonance lines is an important feature in jet-assisted glow discharge atomizers and merits careful consideration in the application of these devices to analytical measurements.

CHAPTER 2

ATOMIC LINE PROFILES IN HOLLOW CATHODE LAMPS AND A GLOW DISCHARGE ATOMIZER DETERMINED BY FOURIER TRANSFORM SPECTROMETRY

2.1 INTRODUCTION

Temperature is an important parameter which controls the characteristics of a plasma. In general, for a monatomic gas, four "types" of temperature exist: (i) the electron temperature, which is characterized by the kinetic energy of the electrons; (ii) the gas (kinetic or Doppler) temperature, which is characterized by the kinetic energy of the heavy particles (atoms, ions); (iii) the excitation temperature, which describes the population of various energy levels; and (iv) the ionization temperature, which describes ionization equilibria [114]. If all the above temperatures have the same numerical value, the plasma is said to be in thermal equilibrium. The mechanisms of analytic excitation given in Table 1, Chapter 1, are described by double-headed arrows, indicating that these parameters of the plasma are in equilibrium. Such a situation is known as thermal equilibrium. In thermal equilibrium, all the temperatures described above have the same value. The majority of analytical plasmas cannot be described as being in thermal equilibrium because there is always a net transport of energy and mass through the system which results in an inhomogeneous temperature distribution [114]. They are more frequently characterized as being in a state of local thermal equilibrium (LTE). This arises when the rate of transport of energy and mass through the system is sufficiently small

compared to the rate at which energy is partitioned over the different degrees of freedom that a state of thermal equilibrium is established in separate volume elements within the plasma which are then said to be in LTE [114].

Glow discharge sources, particularly at low pressure, are not likely candidates to approach LTE conditions due to their low operational pressures and electron densities. Indeed, comprehensive diagnostic studies of glow discharge devices have revealed them to be non-LTE sources in which electron temperatures, ionization temperatures, gas (kinetic) temperatures and excitation temperatures each have their own distinct values [3,22,47,48]. Such a condition is not at all disadvantageous to the analytical utility of these devices. Indeed, in such non-LTE sources many high-lying energy levels may be efficiently excited through selective excitation collisions and charge or energy exchange collisions with excited particles. Additionally, owing to this selective excitation capability, the spectral background of non-LTE sources is often greatly simplified over LTE sources. Furthermore, their low gas (kinetic) temperatures simplifies both cell construction requirements and operation.

It is in part due to their non-LTE character that glow discharge sputtering cells are being used increasingly for direct solids elemental analysis in many fields of atomic spectrometry [2-4,9-12,16,17,92]. Applications of glow discharges as atomizers in atomic absorption spectrometry (AAS), however, raise some practical analytical concerns because the low operational pressure of these devices produces substantial reductions in Doppler and Lorentz broadening relative to atmospheric pressure flame or furnace-based atomizers [98,115-117]. Because of this, glow discharge AAS would be expected to exhibit a greater

dependence on the operating conditions of the primary source and the spectral properties of the analysis line than conventional (thermal) AAS. Thus, Bernhard [92] and Chakrabarti *et al.* [9,10] have found that operation at low lamp currents improved analytical sensitivity. Piepmeier [98,115] provided a detailed theoretical examination of calibration curves in glow discharge AAS. In the absence of self-absorption and/or widely separated hyperfine components and assuming equivalent emission and absorption linewidths he concluded that the slope (sensitivity) at the low absorbance end of the calibration curve would be enhanced relative to atmospheric pressure flames or furnaces due to better overlap between the emission and absorption line profiles. Additionally, improvements in signal-to-noise ratio (SNR) may accrue for glow discharge AAS. For the shot- and/or detector-noise-limited case, O'Haver [25] has calculated that emission/absorption width ratios of 1-2 yield a SNR advantage over classical "narrow-band" AAS. Linear dynamic range, however, would be reduced, producing more pronounced curvature at higher absorbance values [98,115].

The shape of an analytical calibration curve is, of course, affected not only by the linewidths in the atomizer and the primary source, but also by the degree of self-absorption/reversal in the primary source and by the extent of hyperfine and/or isotope splitting of the analysis line. Gilmudtinov *et al.* [118] have shown that the separation of hyperfine components strongly influences the shape of the analytical calibration curve. Calibration curves constructed using analysis lines having widely-separated hyperfine components were found to deviate more from linearity at lower absorbance values than curves which were constructed using analysis lines having closely-spaced hyperfine

components [118]. In a recent experimental study on the effects of hollow cathode lamp profiles on calibration curves in flame AAS, Larkins demonstrated that self-absorption/reversal can be significant for some analysis lines even at low lamp currents, resulting in marked curvature of the calibration graph [119]. For glow discharge AAS, the extent to which hyperfine structure, self-absorption broadening and hollow cathode lamp current influence the sensitivity and linear dynamic range of the analytical calibration curve will ultimately be governed by the relative kinetic temperatures within the hollow cathode lamp and the glow discharge atomizer. Although gas kinetic temperatures of hollow cathode lamps have been shown to vary somewhat with lamp geometry and manufacturer [120,121], the extensive work already performed in this area [104,120-124] suggests a good estimate of the average working lamp gas temperature to be of the order of 550 K [118]. In contrast to the large amount of information available for hollow cathode lamps, data on gas temperatures in glow discharge atomizers are far less plentiful and no consensus on an "average" operating temperature exists. Published values exhibit little conformity, varying from 320-3000 K, depending on the atomizer and operating conditions, sample type, thermometric species and method of measurement [104,125-130].

Although the effect of hollow cathode lamp current on line profiles and the shapes of analytical calibration curves in flame AAS has been studied extensively [104,113,119-124,131-134], most of these investigations were carried out using Fabry-Perot interferometers which have a lower wavelength limit of about 330 nm. This precludes the determination of most of the commonly-used resonance lines in analytical atomic spectrometry. Line profiles in the ultraviolet have been obtained by Zeeman scanning

[135-138], but this approach is limited to resonance lines which show a simple Zeeman triplet. Larkins utilized a high resolution échelle monochromator in the UV to obtain profiles of emission lines from hollow cathode lamps [113,119,131,132] and absorption lines in atmospheric pressure flames [119]. For high-resolution work, however, dispersive grating spectrometry can be complicated by the requirement for a very large diffraction grating or a predisperser and the need for a small slit width, which significantly limits the maximum achievable transmission efficiency. Additionally, dispersive grating spectrometers can have relatively broad instrument (slit) functions, which may be comparable to the widths of the analysis lines in low pressure sources.

Because of its wide spectral coverage, extremely high resolving power, relatively high throughput and the fact that the instrument function is small and can be readily accounted for, Fourier transform (FT) spectrometry has emerged as a particularly attractive tool for line profile analysis [111]. Many applications of FT techniques to plasma-based atomic emission sources have been reported [139-150]. Operation in the ultraviolet, however, poses substantial challenges for FT spectrometry. In particular, the flicker and shot noise associated with many plasma sources becomes redistributed through the Fourier transformed spectrum. This causes a decrease in the signal-to-noise ratio, particularly for weak lines and an increase in limits of detection, resulting in the so-called multiplex or Fourier disadvantage [111]. In contrast to sources such as the inductively-coupled plasma, hollow cathode and glow discharge sources are characterized by their low noise, making them attractive to FT spectrometry [111,151]. Although FT spectrometry has already been applied to glow discharges [151-156], a detailed experimental

investigation has yet to be undertaken which examines the effect of instrumental parameters on line profiles in primary sources and in glow discharge atomizers applied to AAS.

The purpose of the present work is to examine line profiles in commercial hollow cathode lamps and a glow discharge atomizer using Fourier transform spectrometry in an attempt to investigate the implications of using a glow discharge in AAS. Following the terminology of Gilmutdinov *et al.* [118], three groups of analysis lines were investigated: (i) "ordinary" lines having little or no hyperfine and/or isotope structure; (ii) "quasi-ordinary" lines consisting of a group of closely-spaced hyperfine and/or isotope components; and (iii) lines of widely-separated hyperfine and/or isotope components. One representative line from each group was selected. The Mg I 285.21 nm line was chosen as being representative of an "ordinary" line, the Al I 308.22 nm line was chosen to represent a "quasi-ordinary" line and the Pb I 283.31 nm line was selected to represent a line with widely separated hyperfine and isotope components. Profiles of emission lines from commercial hollow cathode lamps were obtained as operating current was varied. Kinetic (Doppler) temperatures in the hollow cathode lamps were obtained from profiles of the aforementioned metal atom lines and, in the glow discharge, from profiles of the Ar I 415.86 nm line. Corresponding absorption profiles of the metal atom lines were then obtained in the glow discharge under typical operating conditions using hollow cathode lamps as primary sources.

2.2 EXPERIMENTAL

2.2.1 Instrumentation.

A Bomem DA3.002 Fourier transform spectrometer (Bomem, Inc., Vanier, PQ, Canada) equipped with a PDP-11/73 minicomputer and high-speed vector processor was used throughout. This instrument is capable of providing unaliased spectral coverage into the vacuum ultraviolet. No aliasing, or deliberate undersampling of the interferogram, was employed in this work. For minimum distortion of spectral features, boxcar apodization was used in all experiments. The maximum (boxcar) apodized resolution attainable with this instrument is 0.004 cm^{-1} . The resolution utilized for the measurement of the Mg I 285.21 nm and Al I 308.22 nm line profiles was 0.050 cm^{-1} , corresponding to a resolution of 0.41 pm at 285.21 nm and 0.47 pm at 308.22 nm, respectively. The Pb I 283.31 nm and Ar I 415.86 nm line profiles were obtained at a resolution of 0.040 cm^{-1} ; this corresponds to a resolution of 0.32 pm at 283.31 nm and 0.69 pm at 415.86 nm, respectively. A 1.5-mm diameter entrance aperture on the instrument was used. A minimum of 15 interferograms were acquired and co-added for each spectrum obtained. Since the time required to obtain a single interferogram was approximately 1 minute, the minimum total analysis time was 15 minutes. Single-sided interferograms were collected, numerically filtered and phase corrected in real time by the Bomem high-speed vector processor. The phase was measured and stored prior to the collection of the analytical interferogram using a 150-W Xe arc lamp as a continuum source. A Hamamatsu R166 solar-blind photomultiplier was used for all experiments except those involving the Ar I

415.86 nm line, for which a Thorn EMI 9801 photomultiplier was used. Both photomultipliers were powered by a Kepco ABC 1500 V regulated dc power supply. To minimize the noise contribution to the spectrum, the spectral bandpass was restricted through the use of interference filters placed in front of the photomultiplier. Melles-Griot interference filters having a full-width at half maximum (FWHM) of 10 nm were used to obtain spectra for all transitions but the Ar I 415.86 nm line. The Mg I 285.21 nm and Pb I 283.31 nm lines were isolated using an interference filter with a peak maximum of 280 nm. A filter having a peak maximum of 320 nm was inclined at an angle of approximately 25° to isolate the Al I 308.22 nm line. A Corning 7-59 glass colour filter having a transmission range of 316.4 - 421.9 nm was used for the measurement of the Ar I 415.86 nm line.

A detailed description of the glow discharge source used in this work has been provided in the previous chapter and, consequently, will only be summarized briefly here. The design is based on the commercially-available Atomsource atomizer [92] which utilizes a configuration in which the discharge gas impinges on the sample cathode through six high-velocity gas jets. This basic design has been modified to permit independent control of discharge gas pressure and flow rate [11] through the use of a mass flow controller (Sierra Instruments model No. 841-07-1, Carmel Valley, CA, USA) mounted on the inlet gas line to control and measure the inlet gas flow rate and Whitey ball valve on the outlet vacuum gas line for pressure regulation. The pressure was monitored on the outlet line to the vacuum pump using a Pirani gauge (Granville-Phillips Convector Gauge, model No. 275, Boulder, CO, USA). A two-stage vacuum pump (Edwards High

Vacuum, model 5, Crawley, Sussex, England) was used. The atomizer was powered by an Advanced Energy Industries, Inc. Model MDX-1K dc power supply (Ft. Collins, CO, USA) operated in constant power mode.

For measurements of the emission line profiles, Westinghouse hollow cathode lamps were used as sources (Ne filler gas). The lamps were operated in continuous (*i.e.*, non-modulated) mode, using a power supply from a Varian Techtron AAS atomic absorption spectrometer (Techtron Pty. Ltd., Melbourne, Australia).

2.2.2 *Materials.*

High purity Ar (99.995%; Liquid Carbonic, Inc., Scarborough, ON, Canada), which had been passed through a moisture trap (Chromatographic Specialties, Model MT120-4) and a particulate filter (Matheson Gas Products) was used as the discharge gas. Measurements of the Mg I 285.21 nm and Pb I 283.31 nm absorption line profiles were obtained by sputtering blocks (3 x 3 x 1cm) of bulk aluminum and leaded brass, respectively. The Al I 308.22 nm absorption line profile was obtained by sputtering a CANMET (Energy, Mines and Resources Canada, Ottawa, ON, Canada) zinc-aluminum reference foundry alloy, NZA-5 (5-cm diameter disc with 1.2-cm thickness), which is certified to contain $10.85 \pm 0.11\%$ Al. Kinetic temperatures were also obtained for the three cathode materials from measurement of the Ar I 415.86 nm emission line profile. All sample cathodes were polished to a smooth surface with 400-grit emery paper on an electric sander, cleaned with ethanol and air-dried prior to use.

2.2.3 Procedures.

Radiation from the hollow cathode lamps was focused through a 150-mm bi-convex quartz lens to a 3 x 3 mm diameter spot size in the central cross-section of the glow discharge atomizer, approximately 20 mm from the cathode surface. Light exiting the glow discharge atomizer was then focused onto the iris of the Fourier transform spectrometer with a second 150-mm quartz bi-convex lens. To achieve the desired resolution the diameter of the spectrometer iris was kept at 1.5-mm. Measurements of the hollow cathode lamp line profiles were made with the glow discharge off as the lamp current was varied from 1 to 30 mA. All lamps were allowed to stabilize for 10 minutes at the desired current prior to the acquisition of a spectrum. Kinetic temperature measurements were made at the same sampling position in the atomizer with the glow discharge operated at the desired conditions (see later). Absorption profiles were obtained as follows: (i) the profile of a line from the hollow cathode lamp was obtained at the desired lamp current with the atomizer turned off; (ii) the profile of the line from the hollow cathode lamp transmitted through the glow discharge was obtained at the same lamp current and the desired operating conditions for the glow discharge; (iii) the background emission profile from the glow discharge was obtained with the hollow cathode lamp turned off. After the transmitted profile was corrected for background emission, a plot of absorption coefficient versus wavenumber could be obtained.

The glow discharge atomizer was operated in constant power mode over a range of 5 to 50 W. The discharge gas pressure was varied from 6 to 15 torr and the gas flow

rate range was 0.3 to 1.2 (standard) L min⁻¹. A stabilization time of 1 minute was used prior to the acquisition of a spectrum. The actual conditions used for a given absorption profile represented compromises between providing a sufficiently high sputtering rate for a given cathode while at the same time minimizing background (glow discharge) emission.

Data from the Fourier transform spectra were then converted into ASCII format and transferred to an IBM-compatible personal computer for line profile analysis. The experimental data points were fit to Voigt profiles (which are convolutions of Gaussian and Lorentzian profiles) using a commercial peak analysis software package (PeakFit, Version 2.01, Jandel Scientific, San Rafael, CA, USA). This program uses the method of Puerta and Martin [157] to approximate the Voigt function and the Marquardt-Levenberg fitting algorithm for convergence. For determination of the kinetic temperatures, the software was used to extract the Doppler linewidth from the fitted profiles. The contribution of the Fourier transform spectrometer instrument function, obtained from the FWHM of the sinc function at the iris diameter used to obtain the interferogram, was then subtracted from the Doppler widths. The resulting Doppler FWHM (hereafter referred simply to as FWHM) was then used to determine the kinetic temperature according to the fundamental relationship:

$$\Delta\sigma_D = \frac{2\sigma_o}{c} \sqrt{\left(\frac{2\ln 2}{M} RT\right)} \quad (2.1)$$

where T is the temperature in Kelvin, R is the universal gas constant, c is the velocity of light, M is the atomic mass in amu, $\Delta\sigma_D$ is the width at half-maximum of the Doppler-broadened line in cm⁻¹ and σ_o is the central frequency of the peak maximum in cm⁻¹.

2.3 RESULTS AND DISCUSSION

2.3.1 Magnesium Hollow Cathode Lamp Line Profile.

The Mg I 285.21 nm resonance line consists of three isotope components [158]: ^{24}Mg (79%), ^{25}Mg (10%) and ^{26}Mg (11%). The latter two components are shifted to lower wavenumbers (higher wavelengths) from the dominant ^{24}Mg line by 0.024 cm^{-1} and 0.047 cm^{-1} , respectively [158]. Because of the small magnitude of this shift and the weak intensities of the ^{25}Mg and ^{26}Mg isotopes, the Mg I 285.21 nm line may essentially be regarded as a single-component or “ordinary” line [118] with reasonably good accuracy. A calculated profile for this line is given in Figure 14, whereas the experimentally-obtained line profiles are shown in Figures 15-17. At a lamp current of 1 mA, the Mg I 285.21 nm line profile is essentially free from self-absorption, as indicated by the good agreement between the fitted Voigt profile and the experimental data points (Fig. 15). The FWHM of this line is 0.090 cm^{-1} , corresponding to a kinetic temperature of 320 K. This is to be expected for a lamp running at low current [123]. The kinetic temperatures measured for the hollow cathode lamp sources used in this work are listed in Table 2. The precision of all the FWHMs in Table 2, indicated by the standard deviation of triplicate recordings of the line profiles, is $\pm 0.0016\text{ cm}^{-1}$. This corresponds to an uncertainty in the measured kinetic temperatures of approximately $\pm 20\text{ K}$. As the lamp current is increased to just 2 mA, however, minor self-absorption occurs, as evidenced by the slightly “flat-topped” appearance of the experimental data points in comparison to the fitted profile (Fig. 16). The FWHM of this line is 0.122 cm^{-1} , corresponding to a kinetic temperature of 570

Figure 14. Calculated profile of the Mg I 285.21 nm resonance line as a function of wavenumber (σ , in cm^{-1}) showing the isotope structure [159].

Figure 15. Profile of the Mg I 285.21 nm resonance line at a lamp current of 1 mA. The dots are experimental data points and the solid line is a fit of these data to a Voigt profile.

Table 2. Gas kinetic temperatures in the hollow cathode lamps.

Analysis Line	Lamp Current (mA)	Doppler FWHM (cm ⁻¹)	Kinetic Temperature (K)
Mg I 285.21 nm	1	0.091	320
Mg I 285.21 nm	2	0.122	570
Al I 308.22 nm	5	0.104	540
Al I 308.22 nm	7	0.105	550
Al I 308.22 nm	15	0.116	670
Al I 308.22 nm	30	0.130	840
Pb I 283.31 nm	2.5	0.032	330
Pb I 283.31 nm	10	0.039	490
Pb I 283.31 nm	15	0.043	600
Pb I 283.31 nm	25	0.050	810

Figure 16. Profile of the Mg I 285.21 nm resonance line at a lamp current of 2 mA. The dots are experimental data points and the solid line is a fit of these data to a Voigt profile.

Figure 17. Profiles of the Mg I 285.21 nm resonance line at lamp currents of 5, 10 and 20 mA. The dots are experimental data points and the solid line is a fit of these data to Voigt profiles.

K, although it should be noted that the small degree of self-absorption observed may introduce a slight high-temperature bias to this result. Above 2 mA, self-absorption/reversal effects dominate the line profile because of the high sputtering efficiency of Mg from the hollow cathode and relatively high oscillator strength of the Mg I 285.21 nm transition [106,119,160]. Self-reversal begins to occur at a lamp current of 2.5 mA (not shown) and intensifies from 5 to 20 mA (Fig. 17). The resulting half-widths across the self-reversed profiles are 0.245 cm⁻¹, 0.318 cm⁻¹ and 0.392 cm⁻¹ for lamp currents of 5 mA, 10 mA and 20 mA, respectively. Similar behaviour for the Mg I 285.21 nm line was observed by Larkins [119] using dispersive grating spectrometry and by Van Heek [136] using Zeeman scanning. These data explain the results of Chakrabarti *et al.*, who found that optimal sensitivity in the determination of Mg in solution residues by glow discharge AAS was achieved at hollow cathode lamp currents of 0.5-1 mA [9,10]. It should be noted that the lamp currents at which self-absorption and self-reversal begin for the Mg I 285.21 nm line (≥ 2 mA) are 10-fold lower than the maximum current recommended by the manufacturer and probably well below the typical currents at which the lamp would be operated in analytical practice.

For flame AAS, Larkins [119] has shown that Mg calibration curves exhibit progressively decreasing slopes (sensitivities) and greater deviations from linearity as lamp current is increased from 3 to 5 mA. In this range the Mg I 285.21 nm line begins to undergo substantial self-reversal broadening. The magnitude of these effects would be significantly exacerbated in glow discharge AAS if the absorption linewidths in the glow discharge were comparable to those in the hollow cathode lamp. Assuming equivalent

emission and absorption linewidths in glow discharge AAS, a lamp current of 1 mA would be expected to produce a calibration curve having a steeper linear portion and greater curvature at high absorbance values than in flame AAS. Operation at higher currents, however, would produce progressive decreases in the slope of the curve and greater curvature at higher absorbances than observed for flame AAS [119]. Furthermore, although the width of the self-reversed Mg line was found never to exceed the width of the absorption line profile in an air-acetylene flame [119], this situation may not hold for glow discharge AAS, producing even more pronounced curvature and reduced sensitivity (slope) at higher lamp currents.

2.3.2 Aluminum Hollow Cathode Lamp Line Profile.

The Al I 308.22 nm line consists of six hyperfine components, spaced approximately 0.01 cm^{-1} apart, which are unresolved so that the profile appears as a single-component line [118]. A calculated profile for this line is shown in Figure 18. The experimentally determined Al I 308.22 nm line profiles are shown in Figures 19 and 20. For both low (Fig. 19) and high (Fig. 20) lamp currents the Al I 308.22 nm line profile is essentially devoid of self-absorption. At 5 mA the FWHM is 0.104 cm^{-1} , which corresponds to a gas kinetic temperature of 540 K. Increasing the lamp current to 7, 15 and 30 mA causes the FWHMs to increase to 0.105, 0.116 and 0.130, respectively. These correspond to gas kinetic temperatures of 550, 670 and 840 K, respectively. These temperatures are in line with the expected gas kinetic temperatures from hollow cathode

Figure 18. Calculated profile of the Al I 308.22 nm resonance line as a function of wavenumber (σ , in cm^{-1}) showing hyperfine structure [118].

Figure 19. Profiles of the Al I 308.22 nm resonance line at lamp currents of 5 and 7 mA.

The dots are experimental data points and the solid line is a fit of these data to Voigt profiles.

Figure 20. Profiles of the Al I 308.22 nm resonance line at lamp currents of 15 and 30 mA.

The dots are experimental data points and the solid line is a fit of these data to Voigt profiles.

lamps at the respective currents [123]. The maximum current recommended by the manufacturer for this lamp is 20 mA. The essential absence of self-absorption in the Al I 308.22 nm line profile suggests that the Al I 308.22 nm calibration curve would exhibit a greater linear dynamic range than the Mg I 285.21 nm calibration curve, most closely approximating the ideal case for a glow discharge AAS source described by Piepmeier [98,115]; that is, a steeper initial slope and earlier curvature than those obtained for atmospheric pressure flames or furnaces. The degree to which this "ideal" behaviour is observed in practice would, of course, depend upon the magnitude of the corresponding absorption linewidth in the glow discharge. This will be considered later.

2.3.3 Lead Hollow Cathode Lamp Line Profile.

The Pb I 283.31 nm line is made up of five distinct components owing to hyperfine and isotope splitting. In order of increasing wavenumber (decreasing wavelength), the isotope components are ^{207}Pb (22.1%), ^{204}Pb (1.4%), ^{206}Pb (24.1%) and ^{208}Pb (52.4%). A calculated profile for this line appears in Figure 21, whereas the experimentally-obtained line profiles are given in Figures 22 and 23. At 2.5 mA (Fig. 22) the line is essentially free from self-absorption and four of the five hyperfine and isotope components are resolved. The ^{204}Pb component, however, is too weak in intensity to be distinguished from the baseline noise. Because only the ^{207}Pb component at 35297.18 cm^{-1} is completely resolved, its FWHM was used for the determination of gas kinetic temperatures. At 2.5 mA this half-width is 0.032 cm^{-1} , corresponding to a gas kinetic temperature of 330 K.

Figure 21. Calculated profile of the Pb I 283.31 nm resonance line as a function of wavenumber (σ , in cm^{-1}) showing the isotope and hyperfine structure [118,132,138].

Figure 22. Profile of the Pb I 283.31 nm resonance line at a lamp current of 2.5 mA. The dots are experimental data points and the solid line is a fit of these data to Voigt profiles.

Figure 23. Profiles of the Pb I 283.31 nm resonance line at lamp currents of 10, 15 and 25 mA. The dots are experimental data points and the solid line is a fit of these data to Voigt profiles.

As lamp current is increased to 5 mA (not shown), some self-absorption of the ^{208}Pb line begins. This is to be expected from the greater concentration of this component relative to the other isotopes. As lamp current is increased to 10 mA (Fig. 23), the overall linewidth increases and there is greater self-absorption of the ^{208}Pb line. The ^{207}Pb and ^{206}Pb components also begin to exhibit self-absorption, as evidenced by the difference in the ratios of the heights of these components relative to the low current case (Fig. 22). The FWHM of the resolved ^{207}Pb component is 0.039 cm^{-1} , corresponding to a gas kinetic temperature of 490 K. At 15 mA self-reversal of the ^{208}Pb component begins and the overall width of the entire line profile increases, yielding a ^{207}Pb half-width of 0.043 cm^{-1} and a gas kinetic temperature of 600 K. At 25 mA self-absorption of the minor Pb isotope components increases, as evidenced by the smaller increase in peak intensity from 15 mA to 25 mA relative to the intensity increase observed when lamp current was raised from 10 mA to 15 mA. The half-width of the ^{207}Pb line is 0.050 cm^{-1} , corresponding to a gas kinetic temperature of 810 K. The maximum current recommended by the manufacturer for this lamp is 8 mA. These general trends in the response of the Pb I 283.31 nm line profile to changes in lamp current obtained in this work are similar to those observed by Larkins [131] using dispersive spectrometry, although the onset of self-reversal was lower (10 mA) in his work. These discrepancies are likely attributable to differences in the construction or age of the lamps used (Westinghouse in this work versus Hamamatsu TV Co. lamps in the previous study [131]).

In the absence of self-absorption, due to its broadly-spaced isotope components, the Pb I 283.31 nm line would be expected to yield analytical calibration curves having

reduced slope and greater curvature at high absorbance values than lines with simple hyperfine/isotope splitting (*i.e.*, "ordinary" or "quasi-ordinary" lines [118]). At low lamp current, where self-absorption is not significant, the Pb I 283.31 nm line would be expected to produce an analytical calibration curve having a shorter linear dynamic range and reduced slope than either of the other two transitions investigated in this study, Mg I 285.21 nm and Al I 308.22 nm. As lamp current is increased and both Doppler and self-absorption broadening increase, the linear dynamic range and slope would decrease even further. An additional practical consideration for glow discharge AAS is the overall width of the components of the Pb I 283.31 nm emission line which, at higher lamp currents, could exceed the absorption linewidth in the glow discharge atomizer, further degrading sensitivity and linear dynamic range.

2.3.4 Gas Kinetic Temperatures in the Glow Discharge.

It is well-known that calibration curves will exhibit greater deviations from linearity and reduced slope (sensitivity) when the emission linewidth exceeds the absorption linewidth. This situation has been shown to occur for sources such as atmospheric pressure flames with certain elements and primary source conditions [119]. The extent to which this situation will exist in glow discharge AAS will be governed predominantly by its gas kinetic temperature. The gas kinetic temperature of the glow discharge will, in turn, depend primarily on the operating conditions of the device (*i.e.*, applied power, voltage or current, discharge gas pressure and flow rate). There may also be a small

dependence on the sample matrix, since different sample materials may conduct the heat generated by Ar^+ bombardment during sputtering to varying extents.

Kinetic, rotational and vibrational temperatures have been measured previously for several types of glow discharge sources by a number of workers [104,125-130] and values ranging from 320-3000 K have been reported, depending on the discharge type, thermometric species, sample composition, operating conditions and observation zone in the plasma. Of particular interest is the work of Ferreira *et al.* [125], who observed a spatial component to gas kinetic temperatures in a Grimm-type glow discharge. The kinetic temperatures calculated from a support gas line progressively decreased with increasing distance from the cathode surface. Kinetic temperatures determined using the Ar I 415.86 nm line were found to vary from 1820 K at a distance of 0.25 mm from the cathode surface to 830 K at a distance of 4 mm from the cathode surface [125]. The maximum values of these temperatures are in good agreement with those of West and Human [104] obtained from end-on viewing of sputtered metal atom lines from the same source. Those from a study by Kuraica *et al.* [128], in which spatially-resolved gas kinetic temperatures of 420-1170 K were calculated from the FWHM of the metastable Ar I 696.54 nm line with side-on viewing of a similar Grimm-type source, are also similar. More recent investigations of other glow discharge sources have yielded different results, however. Ohorodnik and Harrison [127] obtained N_2^+ rotational temperatures of 450-700 K for a non-cryogenically cooled glow discharge source and found that cryogenic cooling reduced these temperatures by between 50 and 100 K. Uzelac and Leis [129] used a diode laser to obtain absorption profiles of Ar I 810.60 and Ar I 811.76 nm lines in a

microwave-boosted glow discharge, from which gas temperatures of 320-520 K were calculated.

To date, no determinations of gas kinetic temperatures in jet-assisted glow discharge atomizers have been reported. These sources have the added complexity that sputtering gas, flow rate and pressure become operational variables in addition to discharge gas power, voltage and current. All of these variables are interdependent and their effects on analyte sputtering rates, absorption and emission signals are complex [11,12,16,17]. The attractiveness of jet-assisted glow discharge sources as atomizers for AAS makes determination of their gas kinetic temperatures of particular interest. Therefore, kinetic temperatures were determined for the glow discharge atomizer for a number of power, pressure and flow rate values for the different sample cathodes used in this study. The use of a support gas line with a suitably low transition probability as a thermometric species has advantages over a sputtered metal atom line in that potential contributions to the line half-width from self-absorption are reduced, thereby enabling the investigation of a wider range of discharge operating conditions and sample types and permitting intercomparison of kinetic temperatures for different cathode materials. Hence, the Ar I 415.86 nm line was used as a thermometric species. This transition has a radiative lifetime of 690 ns [160] and has previously been used for reliable measurements of kinetic temperatures by Ferreira *et al.* [125].

A representative profile of the Ar I 415.86 nm line is given in Figure 24. A good fit of the experimental data points to the Voigt profile was obtained. Kinetic temperatures were derived for a number of glow discharge operating conditions which are listed in

Figure 24. Profile of the Ar I 415.86 nm line from the glow discharge atomizer. The dots are experimental data points and the solid line is a fit of these data to a Voigt profile. A bulk brass cathode was sputtered at a power of 40 W, a flow rate of 0.6 L min⁻¹ and a pressure of 10 torr.

Table 3. The precision of the measured FWHMs, as indicated by the standard deviation of five replicate measurements, is $\pm 0.0013 \text{ cm}^{-1}$, corresponding to an uncertainty of about $\pm 20 \text{ K}$ in the kinetic temperatures. All kinetic temperatures were measured at the same location in the plasma, approximately 20 mm from the cathode surface, in the same analytical volume where the atomic absorption measurements were made. At this point it must be emphasized that the data presented in Table 3 are intended to provide an overview of the magnitude of kinetic temperatures produced in this glow discharge atomizer under analytical operating conditions rather than to serve as a comprehensive guide to the response of plasma kinetic temperature to changes in discharge power, argon gas pressure and flow rate, cathode type and plasma observation zone. Additional constraints on experimental conditions were imposed by the technique used to measure the line profiles and by the bulk composition of the samples investigated. Because 15 minutes was the minimum time required to obtain a Fourier transform spectrum, an effective upper limit of about 40 W was placed on the applied power. This avoided excessive heating of the sample which would bias the measured kinetic temperatures and possibly damage the atomizer body. Additionally, erosion of deep craters in the sample, which can alter the electric field between the anode and sample cathode and physically disturb the plasma, is avoided. As prior work [17,161] has demonstrated that the plasma plume contracts towards the cathode surface at high pressures and/or low flow rates and expands to fill the volume of the atomizer at low pressures and/or high flow rates, the range of pressures and flow rates investigated in this work was restricted to maintain a relatively stable plasma in the analytical sampling zone. Further restrictions were imposed by the aluminum-based

Table 3. Gas kinetic temperatures in the glow discharge atomizer.

Cathode Type	Operating Conditions (power, flow rate, pressure)	Kinetic Temperature (K)
NZA-5 zinc-aluminum	15 W, 0.5 Lmin ⁻¹ , 10 torr	460
Certified Reference	20 W, 0.5 Lmin ⁻¹ , 10 torr	490
Material	10 W, 0.5 Lmin ⁻¹ , 6 torr	460
Leaded brass	40 W, 0.6 Lmin ⁻¹ , 10 torr	510
	40 W, 0.6 Lmin ⁻¹ , 6 torr	520
	40 W, 0.8 Lmin ⁻¹ , 6 torr	510
Aluminum	30 W, 0.5 Lmin ⁻¹ , 6 torr	620
	30 W, 0.5 Lmin ⁻¹ , 10 torr	610
	30 W, 0.8 Lmin ⁻¹ , 10 torr	620
	30 W, 1.2 Lmin ⁻¹ , 10 torr	570

cathode materials used and the argon discharge gas. The presence of oxide layers can cause aluminum to sputter poorly in an argon dc glow discharge. Even if the sample is cleaned scrupulously prior to analysis and the oxide layers are removed, prolonged sputtering at moderate to high powers can result in the formation of an unstable plasma. Therefore, the operating conditions used for the bulk aluminum and NZA-5 zinc-aluminum reference material were further restricted to produce a plasma which would remain stable over the minimum 15-minute analysis time. As a consequence of the different powers used, absolute intercomparisons of gas kinetic temperatures are not possible for any of the three cathode materials used. Notwithstanding these experimental restrictions, several general trends indicated by these data merit discussion. The range of kinetic temperatures for the three different cathode materials is rather small (~ 200 K), indicating that the identity of the cathode has a relatively minor role in affecting the gas temperature of the plasma. A similar conformity in Ar excitation temperatures for a series of different brass cathodes was noted by Fang and Marcus [21]. Even greater similarity exists among the kinetic temperatures for a given cathode type. The temperatures for the NZA-5 zinc-aluminum reference material vary from only 460 to 490 K over the experimental conditions used. The small alteration of pressure and flow rate imparts little change to the kinetic temperatures. A slight increase in the kinetic temperature of 30 K is brought about by an increase in power from 15 to 20 W at a flow rate of 0.5 L min^{-1} and pressure of 10 torr. This is a consequence of the increase in the sputtering rate which accompanies increased power [11,17] and a resulting rise in the heat produced at the cathode surface by Ar^+ bombardment. Temperatures for the brass cathode are similarly uniform (510-520

K) and are slightly higher than the kinetic temperature obtained for the zinc-aluminum alloy, likely as a consequence of the higher discharge power used. The temperatures obtained for the aluminum cathode at a constant power of 30 W change little in the pressure range of 6-10 torr and over the flow rate range from 0.5-0.8 L min⁻¹, varying from only 610-620 K. As the flow rate is increased to 1.2 L min⁻¹, however, the kinetic temperature drops to 570 K. This small decrease is probably a consequence of a distortion in the structure of the plasma at high flow rates rather than being indicative of any significant "cooling" effect exerted on the plasma by the gas jets, as has been suggested by others [16]. At flow rates in excess of 1 L min⁻¹, the plasma expands towards the opposite wall of the atomizer and becomes more diffuse. This would account for the overall decrease in the Ar I 415.86 nm peak intensity observed at these high flow rates and for the small decrease in the measured kinetic temperature.

The kinetic temperatures reported in this work are roughly 300-1300 K lower than those reported using side-on observation of support gas line profiles in Grimm-type glow discharges used by both Ferreira *et al.* [125] at comparable discharge powers and gas pressures (32-64 W and 2-11 torr) and Kuraica *et al.* [128] for lower powers and pressures (9-26 W and 1 torr). Although precise quantitative comparisons between different atomizer types is not possible, the general trend observed in both the above studies that kinetic temperature decreases with increasing distance from the cathode surface likely contributes to the lower kinetic temperatures observed in the present work. The furthest distance from the sample cathode at which kinetic temperatures were measured by Ferreira *et al.* [125] was 4.0 mm, at which the kinetic temperature was found to be 830 K for a 40

W plasma. Kuraica *et al.* [128] reported a kinetic temperature of 800 K at a distance of 7.0 mm for a 15 W plasma. Bearing in mind that kinetic temperatures were measured approximately 20 mm away from the cathode surface in the present study, the results obtained are in reasonable agreement with the previous investigations. Unfortunately, the lack of a micrometer translation stage on our atomizer precluded the acquisition of any spatially-resolved kinetic temperature measurements (the closest approach to the cathode surface is 10 mm because of restrictions in the design of the atomizer). The choice of sampling region was made to coincide with the analysis volume for AAS so that the kinetic temperatures reported in this study would accurately reflect the conditions in the actual environment in which analytical measurements are made.

2.3.5 Comparison of Hollow Cathode Lamp and Glow Discharge Kinetic Temperatures.

For glow discharge AAS, the sensitivity, linear dynamic range and degree of calibration plot curvature are essentially governed by six factors: (i) the degree of self-absorption/reversal in the primary light source; (ii) the separation of hyperfine and isotope components of the analysis line; (iii) the kinetic temperature of the primary source; (iv) the kinetic temperature of the glow discharge atomizer; (v) the amount of stray light entering the monochromator; and (vi) the cross-sectional homogeneity of the atomic vapour. The latter two factors will not be considered in this study. The effects of current on kinetic temperature in the hollow cathode lamp and the degree of self-absorption for analysis lines of different hyperfine and isotope splitting have already been discussed in

this work. The kinetic temperatures obtained for the glow discharge atomizer permit a better analysis of some of the general trends already discussed. In particular, the reduced sensitivity and deviations from linearity already discussed for the Mg I 285.21 nm line purely on the basis of self-reversal of the emission line profile in the hollow cathode lamp would be further exacerbated in glow discharge AAS because of the low kinetic temperature of the atomizer. Using a kinetic temperature of 620 K (since Mg was contained in the bulk aluminum cathode), the FWHM of the Mg absorption line is calculated to be 0.127 cm^{-1} . As is evident from Table 2, this essentially precludes the use of Mg lamp currents in excess of 2 mA for optimum analytical work, although, as already mentioned, this value is 10-fold less than the maximum current rating recommended by the manufacturer. Furthermore, since the half-widths of the self-reversed Mg lines at 5, 10 and 20 mA are 0.245 , 0.318 and 0.392 cm^{-1} , respectively, operation at these lamp currents would cause the emission line half-width to exceed that of the absorption line, further degrading the analytical sensitivity and the linear dynamic range. Using a value of 510 K as being representative of leaded brass would imply that Pb hollow cathode lamp currents of 10 mA and below could be tolerated before the absorption line half-width is exceeded. Operation at lamp currents in excess of 10 mA resulted in self-reversal of the ^{208}Pb component of the Pb I 283.31 nm line. The low kinetic temperature of 330 K arising with a lamp current of 2.5 mA also explains previous work wherein sensitivity was maximized at a lamp current of 3 mA [9]. Analysis of the kinetic temperatures obtained for the NZA-5 zinc-aluminum reference material for the Al hollow cathode lamp indicate that, unlike the case for Mg and Pb, the emission line half-widths exceed those of the

absorption line at all lamp currents. The lowest lamp current examined (5 mA) results in a kinetic temperature of 540 K, which exceeds the maximum gas temperature measured for the NZA-5 cathode by 50 K. This is likely a consequence of the six unresolved hyperfine components of this transition in addition to the increased sputtering efficiency of Al in the Ne fill gas of the hollow cathode lamp. On the assumption of equivalent emission linewidths in the hollow cathode lamps and absorption linewidths in the glow discharge, the lack of self-absorption of the Al I 308.22 nm line would result in calibration curves having greater slope (sensitivity) and linear dynamic range than curves constructed from either the Pb I 283.31 nm line or the Mg I 285.21 nm line. However, because the kinetic temperatures of the glow discharge atomizer are at least 50 K below those of the aluminum hollow cathode lamp, the linear dynamic range and slope of the Al I 308.22 nm calibration curve would be correspondingly reduced. These results also explain why previous work in this laboratory [9] found that optimum sensitivity for aluminum determinations by glow discharge AAS was obtained at a lamp current of 4 mA.

2.3.6 Absorption Profiles.

Although kinetic temperatures provide indirect information on the width of the absorption line profile in the glow discharge, it is still informative to obtain absorption profiles in the discharge directly. Continuum sources such as Xe- or D₂-arc lamps have been used for this purpose in flame AAS [119,121,123,133]. Continuum-source Fourier transform AAS was attempted in this work, but the Xe arc lamp used displayed

considerable flicker and the resulting noise was distributed throughout the transformed spectrum, precluding absorption profile measurement. Additionally, the low (minor) concentrations of the analyte elements present in the available samples mitigated against the success of continuum FT-AAS.

In principle, a plot of absorption coefficient, $k(\sigma)$, versus wavenumber, σ , can be obtained by recording the profile of an emission line before and after absorption and calculating $k(\sigma)$ at discrete intervals along the width of the emission line as follows:

$$k(\sigma) = \frac{1}{l} \ln \left(\frac{I_o(\sigma)}{I(\sigma)} \right) \quad (2.2)$$

where $I_o(\sigma)$ and $I(\sigma)$ represent the emission line intensity as a function of wavenumber before and after absorption and l represents the length of the absorption layer in cm. Wagenaar and De Galan [122] have utilized such an approach to obtain absorption line profiles for the Cu I 324.75 nm, Ga I 403.30 nm and Ag I 328.07 nm transitions in air-acetylene and acetylene-N₂O flames using hollow cathode and electrodeless discharge lamps as sources. The degree to which such an approach can be reliably applied to a glow discharge atomizer will be determined by the kinetic temperatures in the emission source and atomizer. Since the kinetic temperatures of both the hollow cathode lamps and the glow discharge atomizer have been shown to be of comparable magnitude, this approach may be applied to a glow discharge source without significant loss of information from the wings of the absorption line profile.

Figure 25 shows the initial and transmitted profiles for the Mg I 285.21 nm line together with the calculated absorption line profile for a hollow cathode lamp current of

Figure 25. Profiles of the Mg I 285.21 nm resonance line at a lamp current of 2 mA before (●) and after (○) absorption, background emission from the glow discharge (■) and the calculated absorption line profile (— — —). The dots are experimental data points and the smooth line is a fit of these data to Voigt profiles. A bulk aluminum cathode was sputtered at a power of 30 W, a pressure of 10 torr and a flow rate of 0.5 L min⁻¹.

2 mA and glow discharge operating conditions of 30 W, 0.5 L min⁻¹ and 10 torr. These operating conditions should produce kinetic temperatures of 570 and 610 K in the hollow cathode lamp and glow discharge atomizer, respectively. This should be sufficient to record a reasonable approximation of the absorption line profile with only minor losses in the wings. A lamp current of 2 mA was selected as this was the highest current that could be used in the absence of self-reversal. It was desirable to avoid sensitivity losses and possible distortions to the calculated absorption profile from the use of such a self-reversed line. Because the extent of absorption of each component of a self-reversed line can provide useful information on the existence of collisional absorption line shifts [122], the initial and transmitted profiles of the Mg I 285.21 nm line at 20 mA were also recorded (Fig. 26). The degree of absorption for each self-reversed component was essentially the same, indicating no significant collisional line shift of the absorption profile in the glow discharge atomizer.

Figure 27 shows the initial and transmitted profiles for the Al I 308.22 nm line along with the calculated absorption profile for a hollow cathode lamp current of 15 mA and glow discharge operating conditions of 10 W, 0.5 L min⁻¹ and 8 torr. These operating conditions should produce kinetic temperatures of 670 K in the hollow cathode lamp and 460 K in the glow discharge atomizer. In such a case, the width of the hollow cathode lamp emission line is sufficiently large to completely encompass the absorption line, such that no information about the absorption profile would be lost.

The profiles for the Pb I 283.31 nm line before and after absorption at a hollow cathode lamp current of 10 mA and glow discharge atomizer setting of 20 W, 0.5 L min⁻¹

Figure 26. Profiles of the Mg I 285.21 nm resonance line at a lamp current of 20 mA before (●) and after (○) absorption and the background emission from the glow discharge (■). The dots are experimental data points and the smooth line is a fit of these data to Voigt profiles. A bulk aluminum cathode was sputtered at a power of 30 W, a pressure of 10 torr and a flow rate of 0.5 L min⁻¹.

Figure 27. Profiles of the Al I 308.22 nm resonance line at a lamp current of 15 mA before (●) and after (○) absorption, background emission from the glow discharge (■) and the calculated absorption line profile (---). The dots are experimental data points and the smooth line is a fit of these data to Voigt profiles. The CANMET reference foundry alloy NZA-5 was used as a cathode and sputtered at a power of 10 W, a pressure of 8 torr and a flow rate of 0.5 L min⁻¹.

and 10 torr are shown in Figure 28. The calculated absorption line profile is also presented. The kinetic temperature of the hollow cathode lamp at this lamp current is 490 K. That of the glow discharge can be approximated from the data in Table 3 to be somewhat less than 510 K (obtained from Table 3 for a discharge operating at 40 W) owing to the 20 W decrease in the power used to obtain the absorption profile. Thus, the emission and absorption linewidths can be regarded as being approximately equivalent in this case, implying that little information concerning the absorption profile would be lost.

2.4 CONCLUSIONS

The kinetic temperatures of a jet-assisted glow discharge atomizer have been found to be very similar to those of commercial hollow cathode lamps. Clearly, this indicates that the requirement of conventional atomic absorption spectrometry that the emission linewidth be much smaller than the absorption linewidth (one of the conditions of the Walsh atomic absorption method for measurement of the absorption coefficient at the peak centre [41]) is not met when glow discharge atomizers are used. More significantly, the similarity of the kinetic temperatures in the primary source and the atomizer in glow discharge AAS implies that the operating conditions of the glow discharge atomizer and the hollow cathode lamps play critical roles in determining the analytical sensitivity and the linear dynamic range of analytical calibration curves. In particular, the effects of hyperfine structure and self-absorption will be more pronounced in glow discharge AAS than in flame or furnace AAS. In general, low (≤ 5 mA) lamp currents are required to

Figure 28. Profiles of the Pb I 283.31 nm resonance line at a lamp current of 10 mA before (●) and after (○) absorption, background emission from the glow discharge (■) and the calculated absorption line profile (— — —). The dots are experimental data points and the smooth line is a fit of these data to Voigt profiles. A bulk brass cathode was sputtered at a power of 20 W, a pressure of 10 torr and a flow rate of 0.5 L min⁻¹.

decrease the kinetic temperature of the hollow cathode lamp so that it is equal to or less than that in the glow discharge atomizer. Even in the absence of broadening by self-absorption/reversal, the presence of a group of closely-spaced hyperfine components, as with the Al I 308.22 nm line, may produce an emission line whose half-width exceeds that of the absorption line in the glow discharge, further reducing the analytical sensitivity and the linear dynamic range of the analytical calibration curve. Although the results of this study may not be universally applicable to other glow discharge sources, they suggest that the analytical sensitivity and linear range of glow discharge AAS will be significantly degraded if high-intensity primary sources are used, such as electrodeless discharge lamps, because of their higher kinetic temperatures relative to those of hollow cathode lamps.

CHAPTER 3

SPATIAL IMAGING OF STEADY-STATE AND TRANSIENT SPECIES IN THE FURNACE ATOMIZATION PLASMA EMISSION SPECTROMETRY SOURCE

3.1 INTRODUCTION

3.1.1 The Graphite Furnace as an Emission Source

As outlined in the Introduction, attempts have been made to utilize the graphite furnace (GF) as an emission source and exploit the multielement capability that is easily achievable by atomic emission spectrometry (AES) [162-170]. While these excitation sources have the advantage of a small and simple spectral background [23], they are limited by the maximum temperature attainable with the graphite furnace (~3300 K), although operational temperatures of about 3000 K or less are generally preferred to prolong graphite tube lifetime. Consequently, efficient excitation by GFAES occurs only for those elements having excitation energies below that of the high-energy tail of the Maxwell-Boltzmann distribution of thermionic electrons, or below the energies of the Planck distribution for thermal radiation at temperatures near 3000 K [26,49]. This essentially restricts the applicability of GFAES to elements having spectral transitions longer than 300 nm, with correspondingly poor sensitivities being obtained at shorter wavelengths. In general, for transition metals, limits of detection are between 2 and 20-fold poorer when the graphite furnace is used in emission rather than absorption [23]. Although improvements can be made by using an isothermal furnace or a constant

temperature two-step furnace (CTF) [171], they are not sufficient to overcome the inherent sensitivity limitations of graphite furnace atomic emission spectrometry.

3.1.2 Non-thermal Excitation in Graphite Furnaces

Excitation is generally referred to as being “non-thermal” when the line radiance and profile associated with the discharge do not conform to Maxwell-Boltzmann statistics and, hence, cannot be described by any of the LTE models [172]. Non-thermal excitation has been employed for the analysis of discrete liquid samples using Grimm-type glow discharges [6-10,14] and hollow-cathode discharges [173-176]. Samples are typically introduced into the discharge as solution residues on the cathode surface. The analytical throughput of such approaches is, however, compromised by the need for careful cathode preparation and drying of deposited solutions. To circumvent some of the limitations of using glow discharges as the sole means of analyte atomization and excitation, much effort has been made to develop “combined” sources in which the glow discharge plasma is formed within a graphite furnace. In such sources the graphite furnace is used to provide a means of sample atomization into the glow discharge, which then serves as the excitation medium for the thermally-desorbed analyte atomic vapour. Although the volatilization/atomization steps in the graphite furnace should, in principle, be decoupled from the excitation processes occurring in the discharge, the intimate contact between the plasma and the graphite tube makes complete decoupling of excitation and atomization processes problematic.

3.1.2.1 Hollow Cathode Furnace Atomization Non-thermal Excitation Spectrometry

The earliest attempt to form a non-thermal plasma within a graphite furnace was made by Falk and co-workers in the development of Hollow Cathode Furnace Atomization Non-thermal Excitation Spectrometry (HC-FANES) [22,28,32-34]. In this source, the graphite tube itself forms the hollow cathode (held at ground potential) while the anode is composed of a point or ring placed external to the furnace. This arrangement forms a low pressure (1-30 torr) dc hollow cathode discharge in He or Ar, usually operated in a current and voltage regime of 10-100 mA and 300-600 V, respectively. With He, atomic and ionic levels up to 21 eV can be populated, thus extending the applicability of the technique to the entire Periodic Table. Furthermore, because it operates in a sealed low pressure noble gas environment, HC-FANES permits investigation of analytes with transitions in the vacuum ultraviolet. Limits of detection for HC-FANES either exceed, or are of comparable magnitude to, those obtained in GFAAS [28].

A schematic diagram of a typical HC-FANES source appears in Figure 29. The source is based on a Perkin-Elmer Massmann-type tube furnace, which is 28 mm long and has an inner diameter of 6 mm. A commercial instrument based on this design has been manufactured (Fanoquant, Jenoptic JENA, GmbH, Germany) and extensively used in analytical investigations of HC-FANES [177-187]. The HC-FANES discharge is characterized by low gas temperatures, which vary from ~500 K without application of furnace power, to the final temperature to which the graphite furnace (hollow cathode) is ramped. High ionization temperatures (12,000 K for He) and excitation temperatures

Figure 29. Schematic diagram of the Hollow-Cathode FANES source [28].

(10,000 K for He; 8,500 K for Ar at 1 torr) which are essentially independent of applied current over 20-60 mA [28] are achieved. The excitation temperatures decrease with increasing pressure and also increase (by ~ 1000 K) as cathode temperature is increased from 500 K to 2500 K. Electron densities were estimated to be $3 \times 10^{14} \text{ cm}^{-3}$ for Ar and $4 \times 10^{12} \text{ cm}^{-3}$ for He [22]. The increased electron density in HC-FANES relative to planar Ar glow discharges, for which electron densities of between $5\text{--}16 \times 10^{10} \text{ cm}^{-3}$ have been measured [47,48], is the result of the "hollow cathode effect". This is also responsible for the enhanced radiation from the negative glow.

The hollow cathode effect can be visualized by placing two planar glow discharges in close proximity to one another such that the two negative glow regions overlap and coalesce. This coalescence is responsible for producing a current density in a hollow cathode discharge which is several orders of magnitude greater than that for a planar glow discharge at the same cathode fall potential [188]. Electrons entering the glow will be confined there as the result of the retarding field of the opposite cathode, thus losing their energies there through ionizing and exciting collisions. Hollow cathode discharges exhibit a very bright negative glow filling the bulk of the tube, surrounded by a small cathode dark space around the interior cathode walls. A positive column essentially does not form in such a system [189] and the discharge is sustained primarily through photoelectron emission from the cathode surface [188].

The analytical characteristics of HC-FANES depend on the discharge gas, operating pressure and atomization temperature. The first two effects will now be considered. HC-FANES discharges have mainly been established in Ar and He, with the latter affording

excitation of higher energy species such as the non-metals, while the former offers greater electron density. The cell pressure is, perhaps, the most significant operational parameter influencing the structure of the hollow cathode discharge in HC-FANES and, by extension, the generated analytical signals. As pressure is increased, the region of maximum emission intensity shifts from the tube wall to the cathode wall. This is a consequence of the decreased mean free path which causes the bulk of electrons accelerated into the negative glow to dissipate their energies closer to the cathode wall than at low pressures [190]. HC-FANES is predominantly sampled in the centre of the tube to minimize blackbody emission from the furnace walls and no spatial characterization of this source with respect to changes in pressure or plasma gas has yet been reported. Thus, it may be that diminutions in the analytical signal thusfar reported for HC-FANES systems as pressure is changed may possess a significant spatial component which is not yet realized.

Analyte atomization in the HC-FANES source is predominantly thermal in nature. Although cathodic sputtering is responsible for the removal of typically $0.1\text{--}1\ \mu\text{g s}^{-1}$ of sample material at a discharge current of 20 mA, this is negligible in comparison to the rate of mass removal by thermal vaporization ($\sim 1\ \text{mg s}^{-1}$) [28]. Sputtering losses of deposited samples can, however, become more significant if the time between the initiation of the discharge and the start of the atomization cycle is lengthy, particularly if this is done at lower pressures in Ar, as its relatively high mass makes it an efficient sputtering agent. Preatomization losses of Cd have been ascribed, at least in part, to sputtering [187].

The most significant changes affecting the discharge in HC-FANES occur as the source is ramped through a high-temperature atomization step. As the temperature of the

furnace (cathode) increases, emission of electrons from the cathode (furnace) surface are no longer predominantly supplied by photoelectron emission, but by thermionic emission, satisfying the Richardson-Dushman equation for current density (j_e , in Acm^{-2}):

$$j_e = AT^2 \exp \left[\frac{(-e\phi - e\sqrt{eE})}{kT} \right] \quad (3.1)$$

where A is a constant, the theoretical value of which is approximately $120 \text{ Acm}^{-2}\text{K}^{-2}$ [191], T is the surface temperature in K, e is the electronic charge, E is the applied electrical field necessary to account for the influence of external fields on thermionic emission and ϕ is the work function of graphite. Thermionic emission from the graphite tube wall begins at about 1700 K and increases exponentially with temperature, becoming problematic at 1800 K [28]. At 2500 K thermionic effects can become severe because the thermionic emission current can approach several hundred mA. The rapid injection of thermionic electrons into the discharge causes a sharp decrease in the discharge voltage (from 350 to 50 V for an Ar discharge at 4 torr [22]). An asymptotic lower voltage value is reached, regardless of further increases in cathode (furnace) temperature, most likely due to space charge considerations limiting the thermoelectron current. When thermionic emission is dominant, the high-energy tail of the electron energy distribution function essentially disappears [28], leaving only lower energy electrons available for excitation. This significantly decreases the overall excitation capability of the discharge. For these reasons and also to minimize increased diffusional loss at high temperatures, atomization temperatures in HC-FANES systems are generally kept below 1800 K. The low operating

pressures of HC-FANES enables essentially all elements to be volatilized at these low atomization temperatures [28].

3.1.2.2 Hollow Anode Furnace Atomization Non-thermal Excitation Spectrometry

To overcome some of the disadvantages of HC-FANES with respect to thermionic electron emission and to increase the maximum achievable operating pressure (and hence increase atomic residence times), the FANES source was redesigned such that the cathode is no longer the furnace tube wall, but takes the form of a 1-mm outer diameter graphite rod electrode co-axially centred within the graphite tube and traversing its length. Dc power is supplied to the centre electrode (cathode) and the furnace wall. The latter becomes the (hollow) anode in the discharge, held at ground potential. This variant of FANES was given the name Hollow Anode Furnace Atomization Non-thermal Excitation Spectrometry (HA-FANES) [35-38] and it is illustrated in Figure 30. To date, all investigations of HA-FANES have been conducted using a spatially-isothermal 19-mm long integrated contact cuvette (ICC) furnace enclosed inside a 100-mm diameter six-way cross metal chamber, in which pressure is varied. Unlike HC-FANES, where vacuum seals are insufficiently robust to permit discharge pressure to be maintained without a continual flow discharge gas, the pressure vessel which houses the HA-FANES source can be backfilled to the desired pressure and run under “static” gas flow conditions [38]. To date, He and Ar discharges have been established in HA-FANES with optimum pressure conditions for most elements being realized at around 200 torr for Ar and 400-600 torr for

Figure 30. Schematic diagram of the six-way cross vacuum chamber with integrated contact cuvette (ICC) furnace [204]. With dc power applied to the centre electrode, this system has been used as a source for Hollow Anode FANES [35-38].

He [37]. Under these pressure regimes, analyte residence times closely approach those in GFAAS and limits of detection and reproducibility are also comparable to those obtained in GFAAS.

Like its hollow-cathode counterpart, HA-FANES operates in the abnormal glow discharge regime wherein the entire cathode surface is covered by the negative glow. This takes the form of a bright halo surrounding and extending over the entire length of the cathode rod, only partly filling the space between the tube wall and the centre cathode [35]. The negative glow around the centre cathode expands to fill more of the cross-sectional tube volume as discharge pressure is decreased and contracts about the cathode as the pressure is increased [35,38]. This behaviour is the result of the changes in the electron mean free path that accompany changes in pressure, as discussed in Chapter 1. Analyte sputtering does not occur in the HA-FANES source unless the sample is deliberately deposited onto the centre cathode [26,49]. No other luminous glow regions are observed. This is a consequence of the hollow-anode geometry, which has been classified by von Engel as a concentric dc "corona" discharge, (defined as a glow discharge without positive or negative zones, according to whether the centre electrode (wire) is negative or positive [43]).

The current-voltage characteristics of HA- and HC-FANES are different, however. For both systems, graphs of discharge voltage versus discharge current show that voltage increases as current increases, as would be expected for abnormal glow discharges. The magnitude of the increase is ~18 times greater for the HA-geometry [26,49] for the same current. This is a consequence of the electrode asymmetry in that the smaller area of the

centre cathode will carry a greater current density. Additionally, the electric field is strongly dependent upon the source geometry and the breakdown voltage is, in turn, strongly dependent upon the uniformity of the electric field, decreasing as the electric field becomes more non-uniform [26,43,49]. Since the hollow anode geometry produces a highly non-uniform electric field, decreasing hyperbolically from the centre cathode maximum [43], the breakdown voltage for the hollow anode geometry is less than that for the hollow cathode geometry, explaining in part why HA-FANES can operate at pressures more than an order of magnitude above those used in HC-FANES [26,49]. The increased electric field gradient at the centre cathode relative to the weak field approaching the tube wall also explains why the negative glow is of greatest intensity near the cathode surface. The operational pressure of the source will determine the range of discharge currents. A minimum current is required to establish an abnormal glow discharge at a specific pressure and this minimum current increases with increasing pressure. The upper current (pressure) limit is set by arcing between the anode and cathode.

An additional important feature of HA-FANES is the spatial separation of the cathode from the anode wall. Because of this, the centre cathode is only radiationally and convectively heated. Its temperature thus lags behind that of the furnace wall (similar to a L'vov platform effect). Consequently, thermionic emission of electrons from the centre cathode will occur after thermionic emission from the furnace (anode) wall. Although higher atomization temperatures are required in HA-FANES than HC-FANES, due to the higher operating pressure of the former, analytes may be completely volatilized prior to the centre cathode attaining 1800 K where significant thermionic emission occurs.

Chromium has been atomized at 2500 K and 200 torr and its emission signal returns to baseline before a decrease in the discharge potential (due to thermionic emission) is observed [37]. An unfortunate aspect of the spatial electrode separation in HA-FANES and the resultant temperature differential is the occurrence of double peaks in the atomization of analytes [35,37]. This is the result of analyte initially vaporizing from the tube wall, condensing on the cooler centre cathode and then re-desorbing from the cathode once its temperature has increased sufficiently. This effect is most pronounced for involatile elements. A means of minimizing the occurrence of double peaks is to apply a higher current to the centre cathode prior to the atomization step in order to increase its temperature by ohmic heating. At 60 mA the temperature of the centre cathode can exceed 1300°C (orange glow). Operation at these or higher input currents prior to atomization can cause the separation between double peaks to decrease or disappear [37]. This occurs due to a decrease in the temperature lag between the cathode and the furnace wall, as well as heating of the centre cathode such that it is less likely to serve as a primary condensation site.

3.1.2.3 Furnace Atomization Plasma Emission Spectrometry

The tendency for FANES sources to form arcs at high pressure has limited their use to comparatively low pressure (≤ 400 torr) regimes. This restriction results in decreased analyte residence times relative to sources operating at atmospheric pressure. The requirement for reduced pressure operation further complicates the analytical method

and reduces the overall sample throughput attainable. Radio-frequency discharges permit high power inputs at elevated pressure. An rf field is also capable of driving electrons to energies sufficient for ionization if collision-induced reversal of electron motion is in phase with the field [192]. Thus, energy lost by electrons through ionizing collisions can be re-established by primary and secondary electrons through their interaction with the field. In this manner the minimum mean free path between ionizing collisions decreases with increasing operating frequency, with the result that high frequency discharges have lower minimum operating pressures than their dc counterparts [51]. As a consequence, rf power is capable of sustaining uniform, high-density discharges at atmospheric and higher pressures.

The HA-FANES geometry is conducive to the formation of a capacitively-coupled rf plasma in which power is delivered to the centre electrode. Liang and Blades [39] and Sturgeon *et al.* [40] have described such a system, geometrically identical to HA-FANES. The rf plasma was formed in a commercially-available Massmann-type graphite furnace workhead open to the atmosphere rather than in an enclosed ICC system. One of the furnace windows was removed and served as a sleeve for an rf feedthrough containing the 1-mm o.d. graphite centre electrode. The latter terminated a few millimetres short of the length of the 28-mm long Massmann graphite tube. Formation of the plasma in such an “open” environment necessitates the use of a continual flow of discharge gas (typically 200 mL min⁻¹) in the internal volume of the graphite tube [40]. Although this technique could be termed rf-FANES for consistency with its precursors, the differences in the operation of this device, coupled with the uncertainty as to how dominant non-thermal excitation

effects would be at atmospheric pressure and high furnace temperatures, led to this source being named Furnace Atomization Plasma Emission (Excitation) Spectrometry (FAPES). The design described by Sturgeon *et al.* [40] utilizes a modified Perkin-Elmer (Norwalk, CT, USA) graphite furnace power supply and workhead (Model HGA-2200), a diagram of which is presented in Figure 31. Although the initial report by Liang and Blades [39] utilized a modified Thermo Jarrel-Ash (Franklin, MA, USA) graphite furnace power supply and workhead (Model IL655), subsequent investigations in this research group have predominantly featured an ICC furnace enclosed within a laboratory-constructed six-way cross pressure chamber, identical to that used for the HA-FANES source depicted in Figure 30. Recently, a commercial FAPES instrument has become available (Aurora Instruments, Vancouver, BC, Canada), which features an ICC furnace enclosed within a compact workhead [193]. A diagram of this FAPES source appears in Figure 32. Noteworthy aspects of this instrument include a furnace power supply capable of high rates of heating (3500 K s^{-1}) and an rf power supply based on a free-running oscillator. In principle, this should provide a better impedance match than is achievable with fixed frequency quartz crystal rf generators. This commercial source has already been utilized in several investigations of FAPES [194-196].

The FAPES plasma appears as a strong region of emission around the centre electrode with weaker radial emission, terminating in a weak outer plasma formed near the tube walls. This intensity distribution occurs due to the fact that the sheath that develops at each electrode (as the result of the build-up of a positive space charge of He ions) is greater in magnitude at the smaller electrode. This, coupled with the stronger electric field

Figure 31. Schematic diagram of a FAPES source formed in a Massmann-type atomizer [40].

Figure 32. Schematic diagram of the commercially-available FAPES source manufactured by Aurora Instruments, Ltd. [193].

gradient at the smaller electrode, explains why emission from an annulus proximate to the centre electrode dominates the FAPES plasma. The discharge is primarily capacitively coupled to the generator with a blocking capacitor connected in series so that no net current flows through the circuit. This configuration is shown diagrammatically in Figure 33. As the result of the difference in the mobilities of electrons and ions in the plasma and the surface area asymmetry of the FAPES electrodes, a negative dc self-bias potential develops on the smaller powered electrode, which is the centre electrode in this case [197]. This dc-self-bias potential can be visualized as being the magnitude by which the applied rf voltage is offset from a mid-point of zero, as illustrated in Figure 34. As can be seen from Fig. 34 (b), a negative bias voltage will displace the rf voltage waveform such that the centre electrode will behave as a cathode for a greater period of time than the graphite tube during a given rf half-cycle. The more negative the dc bias voltage on the centre electrode becomes, the longer it will act as a cathode for a given half-cycle.

Conversely, if the dc bias is made positive the rf waveform will be displaced such that the centre electrode behaves as an anode for a greater length of time than the graphite tube during a given half-cycle. Zero dc bias will cause both electrodes to behave as cathodes and anodes for equal periods of time. The magnitude of the dc self-bias potential developed in FAPES is more than an order of magnitude less than those developed in low pressure rf glow discharges [77,199-202] owing to the much more rapid thermalization of electron energies *via* collisions that occur at atmospheric pressure. When the FAPES source is operated at room temperature (*i.e.*, in the absence of furnace heating) at an rf input power of 50 W, the self-bias of the centre electrode is nominally -5 to -10 V. This

Figure 33. Schematic diagram illustrating the configuration of rf generator, tuner, blocking box, and dc power supply utilized to control the dc bias potential of the centre electrode [197].

Figure 34. Radio-frequency voltage waveform for a capacitively-coupled load and its variation with the dc bias (V_{dc}) of the powered electrode for: (a) 0 V dc bias; (b) negative dc bias; and (c) positive dc bias. The dashed line represents the actual voltage waveform from the power supply whereas the dashed line represents the peak-to-peak (plasma) potential [198].

value becomes slightly more negative as the electrode thickness decreases due to He^+ bombardment. The most probable explanation for this is that the narrower electrode presents a smaller area to the discharge, forming a larger voltage sheath. The effects of narrow electrodes on excitation conditions in FAPES will be considered later. As the forward power is increased electron density increases [203], with the result that the dc-self bias of the centre electrode becomes increasingly negative with increasing forward power (e.g., -18 V at 100 W and -50 at 150 W [197]).

More important dc self-bias effects are brought about by heating the graphite furnace through an atomization transient. A plot of dc self-bias response to graphite tube temperature is given in Figure 35 for a dry, unloaded furnace in a Massmann-type Perkin-Elmer Model HGA-2200 workhead. The temperature was ramped to 2600 °C in the maximum power heating mode using a Perkin-Elmer Model HGA-500 power supply. At 1.0 s into the heating cycle, the self-bias begins to take an appreciable negative dip in voltage, maximizing at -120 V at ~1.8 s. This is the result of thermionic emission of electrons from the tube wall to the centre electrode. As the flux of thermoelectrons begins to reach the centre electrode, the dc self-bias becomes more negative in an effort to repel it. This flux is independent of the form of the centre electrode and, at the maximum dip in the self-bias potential, an electron current of 220 mA can be measured between the centre electrode and the tube wall [197]. The maximum voltage attained at the self-bias dip (-120 to -125 V) is invariant of the rf forward power. The onset of the dip occurs several hundreds of milliseconds earlier at powers of 100 W and above due to more efficient plasma-induced heating of the centre electrode by He^+ bombardment [197]. As

Figure 35. The variation of dc self bias potential of the centre electrode with time and temperature during an atomization transient. The left hand side trace represents the change of dc bias with temperature, whereas the right hand side trace represents variation in temperature of the graphite tube with time for a 2600 °C atomization under maximum power heating conditions.

mentioned previously, the temperature of the thermally-isolated centre electrode lags behind that of the tube wall (in this case, by ~ 1 s). When the centre electrode temperature reaches ~ 1800 K, thermionic electron emission from its surface begins, creating a space charge of electrons which repels the flux from the walls. As a result, the self-bias potential reverses polarity. When the temperature of the centre electrode and the furnace wall reach equilibrium, the self-bias potential returns to its initial "room temperature" value [197]. Because of the extremes of variation of the dc self-bias during an atomization transient, Sturgeon *et al.* [197] investigated the possibility of dc bias control as a means of affording a more robust environment for analytical measurements. By means of a blocking capacitor (shown in Figure 33) and a dc power supply, the dc bias voltage can be controlled and voltage can be applied to the centre electrode in ± 12 V increments. For a number of analytes in clean matrices, bias control (generally 0 V bias) was found to increase sensitivity and decrease limits of detection [197].

A further consequence of heating the graphite tube is the change in plasma impedance at elevated temperature which, at the high heating rates normally used, occurs too quickly for the autotuning capabilities of the impedance matching network of the rf generator to compensate. This is currently problematic for FAPES because the majority of studies conducted thusfar have employed rf power supplies having fixed-frequency quartz crystal-controlled oscillators. The use of generators based on a free-running oscillator, which change operating frequency to compensate for changes in the load (FAPES) impedance, may alleviate this problem. The commercial version of FAPES (Aurora Industries, Vancouver, BC, Canada) employs such an rf supply, but no provision

for monitoring input and reflected power has been made. Limited studies undertaken with this source [194,195] have not addressed the impact of this parameter on analytical measurements. Generally, reflected powers can be tuned to 0-1 W for forward rf powers up to 200 W, provided that tube wall temperature does not exceed ~2000 K. Beyond this, reflected power increases commensurate with thermionic electron emission from the surface of the centre electrode. At tube wall temperatures of 2900 K or above, reflected power levels approach 65% of forward power. Despite these high reflected power values, which suggest degraded performance, no analytical difficulties have been experienced in FAPES, even at extremes of reflected power.

The FAPES source is not in LTE [203]. Excitation temperatures, using He I as the thermometric species, of the order of 3000 K have been consistently measured in FAPES [197,203]. These temperatures do not change significantly when the reflected power is deliberately detuned to 40 % of forward power [197]. When the forward power in a properly tuned system is increased 4-fold, excitation temperatures increase by only about 25 %, despite the accompanying larger increases in electron density and plasma volume [203]. Similarly, during an atomization transient in which the graphite tube wall is ramped from 600 - 2600 K, the He I excitation temperature increases by only about 20 %. Excitation temperatures measured using Fe and Pb as thermometric species have also been made. Blades and co-workers have measured spatially-resolved Pb excitation temperatures with a charge-coupled device (CCD) camera [196] and Fe excitation temperatures with conventional photomultiplier tube detection [204]. For a 25 W plasma, these authors reported that Pb I excitation temperatures ranged from a maximum of approximately 5200

K near the centre electrode to a minimum of 4600 K 1 mm from the tube centre. Close to the tube wall, a value of nearly 5200 K was recorded [196]. These compare with measured Fe excitation temperatures of 3150 K at 15 W and 4050 K at 50 W obtained previously [204]. In contrast to the data obtained by Blades and co-workers, Sturgeon *et al.* reported much lower mean Fe I excitation temperatures of 2920 ± 180 K for a higher plasma power of 100 W [203]. Most startling in these experiments is the large discrepancy between excitation temperatures obtained by two different research groups possessing identical rf power supplies and matching networks. The exact cause of this divergence is not clear, but it serves to illustrate the non-LTE character of FAPES in that temperature will be dependent upon the chosen thermometric species and the method of measurement.

Sturgeon *et al.* [203] measured the kinetic (gas) temperature in FAPES, estimated from the Doppler profile of the Be I 234.86 nm line, to be 7000 K. This highly unrealistic overestimation likely resulted from the formation of a high-intensity arc between the tube wall and a large deposit of metallic Be that was used to produce a steady-state signal as the line profile was scanned. Le Blanc and Blades [196] measured spatially-resolved OH and N_2^+ rotational temperatures using a CCD camera. These rotational temperatures can be regarded as providing reasonable estimates of kinetic temperatures. In general, the rotational temperatures of both thermometric species exhibited similar spatial responses, reaching ~1000 K near the tube wall, experiencing a small dip to ~700 K two mm away from the central axis of the graphite tube. Near the centre electrode, however, the OH rotational temperature reached a maximum of ~1300 K at 200 W, whereas the N_2^+

rotational temperature was ~3000 K at this rf input power [196]. This discrepancy was ascribed to the contribution of energy to the N_2^+ rotational system from charge transfer with He_2^+ [205]. Using an electron density of $6.7 \times 10^{13} \text{ cm}^{-3}$, measured from the full-width half maximum (FWHM) of the H_β line at 486.13 nm at a forward rf power of 50 W, Sturgeon *et al.* [203] calculated ionization temperatures from the Saha equation for He I, Mg, Fe, Cd and Zn. A He I ionization temperature of 11000 K was calculated, whereas ionization temperatures for the other analytes varied from 4800 - 5900 K [203]. Clearly, this non-conformity of plasma temperatures and the dependence of plasma temperature on thermometric species, is strong evidence for the lack of existence of LTE in the FAPES plasma.

The vast majority of studies conducted with FAPES to date have employed He as the discharge gas and a fixed frequency rf generator at 13.56 MHz [39,40,196,197,203,204,206-217]. Despite its lower ionization potential relative to He, Ar FAPES discharges cannot be reliably ignited or sustained at 13.56 MHz because the ionization rate of Ar is two orders of magnitude less than He [204]. The rate of ion production should increase with operating frequency since electron loss by collision with the tube wall decreases with increasing frequency and electrons can undergo ionizing collisions during more than one half-cycle of the rf field. Increased operating frequency should bring about easier operation in general and Ar plasmas can be ignited and sustained in FAPES at frequencies of 27.12 MHz or greater [195,218]. In a study in which operating frequency was varied from 13.56 - 54.24 MHz with a crystal-controlled oscillator, Sturgeon *et al.* [218] found that increasing operating frequency yielded higher excitation temperatures for both He and

Ar, as well as enhanced line intensities. Owing to increased background with increasing frequency, however, limits of detection were only marginally enhanced with increased operating frequency [218]. For a given rf input power and frequency, Ar excitation temperatures exceed those of He by ~ 200 K and its enhanced analyte residence times, electron number densities and line intensities *vis à vis* He make operation in this gas an attractive alternative to He.

Regardless of which discharge gas is employed, however, FAPES suffers from a highly structured background of molecular gas bands from 200-450 nm, with the preponderance of these transitions occurring in the ultraviolet region [204,209,218]. This is particularly unfortunate since it is in this spectral region that the majority of atomic (analyte) lines also occur. Wavelength traces obtained by Sturgeon *et al.* [209] for a 50 W He plasma at 13.56 MHz are reproduced in Figure 36. They reveal little molecular background from 450 - 700 nm, with the only lines present being those from the discharge gas. Below 450 nm, however, the background is highly structured and contains intense molecular bands from N_2 , N_2^+ , NO, CO^+ and OH, as well as the strong He I 388.86 nm plasma gas line [209]. Similar results were obtained by Hettipathirana and Blades [204] for a Massmann-type FAPES plasma in He at 13.56 MHz. When Ar is used in a Massmann-type configuration the high-lying energy state species CO^+ , N_2 and N_2^+ disappear as the result of the lower excitation levels of Ar with respect to He. However, these features are replaced by the formation of intense CN bands centred approximately at 360 and 385 nm, a strong C I line at 247.9 nm and well-developed C_2 bands at 470 and 515 nm, brought about by much more efficient centre electrode sputtering, heating and

Figure 36. Wavelength scans from 200-700 nm for a Massmann-type He FAPES source operating at a frequency 13.56 MHz and a forward rf power of 50 W. The centre electrode was allowed to self-bias and the tube wall temperature was maintained at 700 K for the duration of the scan [209].

resultant carbon volatilization by bombardment with the more massive Ar ion [218]. The background spectrum is most line-rich when the discharge is formed in a Massmann-type graphite furnace (which is open to the air). Sturgeon *et al.* [218] have observed that use of an enclosed ICC furnace, similar to that used for HA-FANES by Ballou *et al.* [35] and ultra-high purity gas can drastically decrease molecular background to essentially lines from the discharge gas itself, CO⁺ and OH (likely formed from trace impurities in the discharge gas, liberation of carbon *via* He⁺ bombardment of the centre electrode and adsorbed water on the graphite tube surface).

Analyte residence times in FAPES are shorter than those obtained in conventional GFAAS typically because atomization takes place in a He environment rather than in Ar. Although Massmann-type FAPES systems require a continual internal flow of discharge gas (typically 200 mL min⁻¹), decreasing or increasing this flow rate over the regime 75-325 mL min⁻¹ has little effect on analyte residence times, which suggests that emission signals are source function controlled and that the dominant loss mechanism is diffusion from the graphite tube. Limits of detection in FAPES are in the low pg range and, as such, are comparable with both (HC- and HA-) FANES and GFAAS. Precision, as determined by the relative standard deviation of manual sample introduction, ranges from 3-10 % for FAPES, compared with 2-6 % for HA-FANES and 2-3 % for HC-FANES. The linear dynamic range for FAPES is 2-4 orders of magnitude, as compared to the 5-6 orders of magnitude attainable with HC-FANES. This derives from self-absorption of atomic vapour at the cooler ends of the graphite furnace in the plasma. This problem is common to all graphite furnace-based plasma sources, although it should be alleviated

somewhat through the use of an isothermal ICC furnace (which is 9 mm shorter than a Massmann tube). Measuring peak area produces greater linear range than measurement of peak height.

Introduction of analyte vapour into the plasma occurs predominantly from thermal vaporization from the tube wall. FAPES plasmas are normally operated in He, which is a weak sputtering agent owing to its small atomic mass. Atmospheric pressure operation produces mean free paths which would redeposit any sputtered material. Furthermore, because the larger voltage sheath occurs at the smaller electrode, any sputtering in the system would occur at the centre electrode since the smaller voltage sheath associated with the larger electrode (graphite tube wall) is insufficient to provide He with sufficient energy to sputter the tube wall surface. Even when analytes (Ag and Cu) are deposited directly onto the centre electrode and dc bias potentials of -88 V are applied for 150 s followed by atomization into a self-bias plasma, no measurable sputter losses are observed [197]. More problematic for FAPES may be preatomization losses arising from desorption of volatile nonmetals in the He plasma. As an example, significant amounts of phosphorus are lost as PO during a 5 s "plasma stabilization period" in which a 75 W rf plasma was ignited at a tube wall temperature of 300 °C prior to atomization [212]. It was not ascertained unequivocally whether loss of P-O occurred exclusively from thermal desorption as the result of plasma-induced heating, or whether sputtering played a significant role. Use of reduced Pd as a matrix modifier sufficed to inhibit loss of P as PO [212]. More important effects in analyte atomization arise from the presence of the thermally isolated centre electrode whose temperature lags behind that of the tube wall. At low or moderate plasma

powers, double peaks frequently are observed in analyte emission transients [195,215] and have been shown to occur as a result of initial vaporization of atomic or molecular species from the graphite tube wall followed by condensation onto the cooler centre electrode. The latter then serves as a secondary volatilization site when its temperature rises sufficiently. The degree to which this phenomenon occurs is dependent upon the forward rf power (and attendant plasma-induced heating), the volatility of the analyte, the length and thickness of the centre electrode (less massive electrodes heat more readily; additionally, excitation temperatures have been observed to increase in the presence of a shorter electrode [203], thus shorter electrodes may produce a "hotter" plasma), the furnace heating rate and degree of tube isothermality. Double peak effects are more pronounced for ICC-based systems wherein more efficient heating of the graphite tube produces a greater temperature lag between the tube wall and centre electrode, thus exacerbating condensation/volatilization phenomena.

FAPES is a radially inhomogeneous plasma and all monochromator/photomultiplier (PMT) detection systems most commonly used in investigations are capable of isolating only a thin slice of the total plasma volume, usually that which is in closest proximity to the centre electrode. In the geometrically-identical HA-FANES source, Harnly *et al.* [36] obtained integrated emission intensities for Cu and Cd from six different regions surrounding the negative glow ("halo" or "corona" region) around the central cathode using an échelle monochromator and PMT detector. Cadmium emission intensities appeared to be biased more strongly above the centre cathode than below it, whereas Cu emission intensities were both vertically and horizontally asymmetric with

regions of strongest intensity occurring at the top and at one side of the centre cathode [36]. In the FAPES source, Hettipathirana and Blades [204] have obtained spatially-resolved emission intensities of plasma gas species across the width of the graphite tube by translating their source in discrete increments in front of a linear photodiode array detector. Such mapping approaches are, however, limited to the recording of thin strips of information and cannot reliably be used for obtaining spatial and temporal distributions of excited analyte species during an atomization transient, since a series of images of sequential analyte atomizations, which may not be reproducible, would have to be gathered.

A particularly successful approach to the determination of analyte atom distributions within electrothermal atomizers has been the shadow spectral filming technique of Gilmutdinov and co-workers [219-221] in which atomic or molecular absorption across a two-dimensional cross-sectional area of a graphite tube is obtained by recording the attenuation of the primary light source (*i.e.*, hollow cathode or electrodeless discharge lamp) through the atomizer onto 16-mm film at framing rates of nominally 16 frames per second during the course of an atomization transient. This technique has recently been further refined by the replacement of the film camera with a charge-coupled device (CCD) camera as a detector [222], thus permitting near real-time quantitative analysis of either steady-state or transient phenomena.

Recently, Le Blanc and Blades employed a CCD camera and high-resolution échelle monochromator to obtain spatially-resolved measurements of He emission intensity, as well as OH and N_2^+ rotational temperatures, across the volume of an unheated graphite

tube as rf input power was varied [196]. They also obtained spatially-resolved measurements of Pb emission intensity and Pb I excitation temperatures from Pb atomized into the plasma. Unfortunately, these spatially-resolved data were obtained using an integration time of 1.5 s, such that each image was obtained over the course of the entire Pb emission transient. Thus, all the two-dimensional information presented by Le Blanc and Blades [196] is "spatially and temporally averaged" and the time resolution used by these workers is insufficient for the recording of detailed information about the two-dimensional dynamics of excited atom formation and decay attainable with the CCD system of Chakrabarti *et al.* [222].

Obtaining spatially- and temporally-resolved distributions of analyte atoms and plasma gas species within the FAPES source is of importance because strong radial inhomogeneity of the plasma is indicated [204]. Such information would be useful not only for diagnostic purposes but also may serve as an aid to determining an optimal observation point for analytical determinations. Additionally, the FAPES plasma may also be utilized to gain insight into phenomena affecting Massmann-type graphite furnace atomizers in general, such as the ingress and distribution of components of the ambient atmosphere.

3.2 EXPERIMENTAL

3.2.1 Instrumentation

3.2.1.1 FAPES Atomizer

Much of the instrumentation used in this study has been described in detail in previous publications [40,197]. The FAPES workhead consisted of a modified Perkin-Elmer Model HGA-2200 atomizer into which a 1-mm pyrolytic-coated graphite electrode was co-axially centred (Fig. 31). A mount with four set-screws was attached to one end of the furnace housing to permit precision positioning of the centre electrode. Radiofrequency (rf) power is supplied to the centre electrode by an Advanced Energy Industries (Ft. Collins, CO, USA) Model RFX-600 13.56 MHz generator tuned with a Model ATX-600 impedance matchbox. The direct current (dc) bias voltage on the centre electrode was controlled, in approximately 12 V increments, over a range of -88 to +88 V using an rf blocking box (Advanced Energy Industries, Inc., Model 5018-000-C) and seven 12 V motorcycle batteries connected in series [197]. The magnitudes of the bias voltage and the reflected power were read from the appropriate ports on the ATX-600 tuner. A Perkin-Elmer Model 76B graphite furnace controller was used as the furnace power supply. The maximum power heating rate was employed for all analyte atomizations.

The temperature of the graphite furnace was measured with a calibrated Ircon Series 1100 automatic optical pyrometer (Ircon, Niles, IL, USA) focused onto the graphite tube wall through the dosing hole. The output of the pyrometer was collected and stored

on a Nicolet Series 4094 digital oscilloscope (Nicolet Instruments Canada Inc., Mississauga, ON, Canada).

Although pyrolytic-coated graphite tubes (Perkin-Elmer Co., Norwalk, CT, USA) were used for most experiments, a tube coated with a 50- μm layer of pyrolytic boron nitride (Ringsdorff Werke, Bonn, Germany) and a tube fabricated entirely from machinable glass ceramic (Macor; Corning Glass Works, Corning, NY, USA) were also used. A 2.80 x 0.40 x 0.06-cm Macor strip and a 2.50 x 0.50 x 0.05-cm graphite strip, designed to fill the length of a graphite tube, were used as L'vov platforms in some experiments.

3.2.1.2 Imaging Spectrometer

The basic components of the imaging spectrometer have been outlined in a previous paper [222], with the salient modifications being the removal of the primary light source and collimating lens, the replacement of the conventional graphite furnace atomizer with one modified for FAPES [40] and the addition of the rf generator components. A block diagram of the apparatus appears in Figure 37. A Photometrics CH250/A thermoelectrically-cooled camera (Photometrics, Ltd., Tucson, AZ, USA) containing a Thomson TH1883 chip (384 x 576 pixels) was used. The operation of the CCD was controlled by a Photometrics AT200 16-bit camera controller board installed within an IBM-compatible 486/33 microcomputer (33MHz, 80486DX central processing unit). The output of the CCD was digitized by a 500 kHz A/D converter and the resulting 12-bit

Figure 37. Block diagram of CCD imaging spectrometer.

image was displayed using Image200 Image Acquisition Software (Version 2.0.0; Photometrics Ltd., Tucson, AZ, USA).

For obtaining images of steady-state ("static") phenomena in the plasma, such as support gas and background molecular species, the full spatial resolution of the CCD was utilized [223]. A subregion on the chip of sufficient size to contain the image was defined (typically 380 x 280 pixels), an exposure time selected to provide good signal to noise (0.4 to 4 s, depending on the wavelength region) and the camera manually triggered. For obtaining time-resolved images a co-axial cable connecting the "Peak Read" port of the graphite furnace power supply to the serial port of the computer was used to trigger the camera at the start of an atomization cycle. The CCD itself was operated in frame-transfer mode [223], wherein the chip is divided into two regions of equal size. An image is acquired on the lower half of the chip (image array) and then quickly transferred into the upper half of the chip (storage array) for subsequent read-out. To prevent blurring (aliasing) of the image during frame transfer, a variable-frequency chopper is positioned between the atomizer and the focusing lens, with the frequency output of the chopper connected to the AT200 camera controller board. The timing of the frame transfer is controlled by the frequency output of the chopper so that the transfer occurs while the emission from the atomizer is blocked by a chopper blade. The ultimate time resolution of the CCD is limited by its readout rate (typically 200,000 pixels s^{-1}) and, thus, the image size. In order to obtain time resolution sufficient to accurately image FAPES emission transients, the size of the active image array was reduced by the use of 4 x 4 binning in which the output of 4 serial and 4 parallel pixels is combined. Although such an approach

also decreased the spatial resolution of the CCD, the resulting resolution ($\sim 0.01 \text{ mm}^2$) was quite adequate and was similar to that used earlier for the imaging of atomization transients in GFAAS [222]. Emission transients were obtained at a rate of 50 ms per image.

A 1:1 image of the central cross-section of the atomizer interior was formed on the CCD camera by a 150-mm focal length bi-convex UV grade synthetic fused silica lens. Light exiting the lens then passed through an iris diaphragm to provide depth-of-field and an interference filter (Andover Corporation, Lawrence, MA, USA) to isolate the spectral region of interest. The interference filter was mounted in a precision post rotator (Melles Griot, Irvine, CA, USA) attached to the CCD camera by means of a flexible bellows (Ealing Electro-Optics, Inc., Holliston, MA, USA) to prevent stray light from striking the working surface of the CCD. The interference filters used in this study to isolate the desired spectral lines are tabulated in Table 4 along with their associated bandpasses and transmission efficiencies at peak maximum. Table 4 is organized such that the most prominent band of a particular transition is listed first, followed by weaker transitions which fall within the bandpass of the interference filter used. Information on the band system and wavelengths for the molecular species was taken from Pearse and Gaydon [224]. Wavelengths for the atomic lines are from Corliss and Bozman [106] and Reader *et al.* [160]. Data on the energy levels for atomic and molecular systems are from Radzig and Smirnov [225].

Table 4. Spectral features monitored and interference filters used for detection of excited-state helium plasma gas species and silver.

Species	Energy levels (eV)	λ (nm)	Central wavelength and FWHM of interference filter (nm)	Transmission efficiency at peak maximum (%)
He I	21.22 - 23.07	667.82	651 ; 25	62
N ₂ (Second Positive System)	7.38 - 11.05	380.49 (0,2) 371.05 (2,4) 375.54 (1,3) 385.79 (4,7) 389.46 (3,6)	380 ; 10	43
CN (Violet System)	0 - 3.19	388.34 (0,0) 385.09 (4,4) 385.47 (3,3) 386.19 (2,2) 387.14 (1,1)	380 ; 10	43
CO ⁺ (First Negative System)	0 - 5.69	229.96 (0,1) 221.45 (1,1) 222.03 (8,6) 222.27 (5,4) 224.04 (2,2) 225.43 (6,5) 226.86 (3,3) 229.37 (10,8) 229.82 (4,4) 232.52 (1,2) 235.25 (2,3) 236.25 (6,6) 238.15 (3,4)	230 ; 10	12

Table 4. (continued).

Species	Energy levels (eV)	λ (nm)	Central wavelength and FWHM of interference filter filter (nm)	Transmission efficiency at peak maximum (%)
γ -NO (Third Positive System)	0 - 5.45	259.56 (0,3)	260 ; 10	24
		251.64 (2,5)		
		252.36 (2,5)		
		255.00 (1,4)		
		255.90 (1,4)		
		263.07 (2,6)		
		263.91 (2,6)		
		267.14 (1,5)		
		268.00 (1,5)		
OH	0 - 4.05	306.36 (0,0)	300 ; 10	23
		306.72 (0,0)		
		307.80 (0,0)		
		308.90 (0,0)		
		294.52 (3,2)		
		295.12 (3,2)		
		296.24 (3,2)		
Ag I	0 - 3.66	338.29	340 ; 10	32

3.2.2 Reagents

High purity He (99.995%; Liquid Carbonic, Inc., Scarborough, ON, Canada) was passed through the internal purge gas inlet of the graphite furnace at a flow rate of 200 mL min⁻¹ and served as the FAPES plasma gas. High purity Ar (99.995%; Liquid Carbonic, Inc., Scarborough, ON, Canada) was used as the external sheath gas and was maintained at a flow rate of 1 L min⁻¹. A stock solution (1000 mg L⁻¹) of Ag was prepared by the dissolution of the high purity metal in concentrated HNO₃ (Ultrex grade; J.T. Baker Canada, Toronto, ON, Canada), followed by dilution with ultrapure (18.3 MΩ-cm resistivity) distilled, deionized water (DDW). Working standards were obtained by dilution of the stocks with DDW acidified to 1% v/v with HNO₃.

3.2.3 Procedure

For obtaining images of the He plasma and background molecular features (CO⁺, N₂, γ-NO and OH), the furnace power supply was not used and a 50 W plasma was formed while the (unloaded) graphite furnace was at room temperature. The dc bias on the centre electrode was varied to determine its effect on the spatial distribution of the plasma and background molecular species. An exposure time sufficient to provide good signal-to-noise was selected and the CCD camera manually triggered. This procedure was repeated using a boron nitride coated tube and a Macor tube. Spatial distributions of the above plasma gas species were also determined for graphite, boron nitride and Macor tubes into which Macor and graphite strips were inserted.

To obtain images of ingress of the atmosphere into the FAPES plasma a 50 W plasma was first formed with a 0 V dc bias imposed on the centre electrode. The furnace was then ramped from room temperature to 2000°C at a rate of 1250°C s⁻¹. At the onset of atomization, a signal pulse was sent from the peak read port of the furnace controller to the serial port of the computer and the CCD camera triggered automatically. A series of 10 images, each taken with of an exposure time of 1 s, was then successively collected.

Images of FAPES emission transients were obtained as follows. Solutions (10 µL) of 4.0 µg mL⁻¹ Ag were manually pipetted into the atomizer. A 100°C, 30 s drying stage and 400°C, 30 s charring step were used. The graphite tube was then allowed to cool to room temperature and the plasma ignited. The analyte was then atomized at 2700°C (using maximum power heating) for 5 s, after which the rf power was turned off. The CCD was operated in frame transfer mode and a sequence of 100 images was obtained from the onset of the atomization trigger. The analytical line monitored and interference filter used for Ag are listed in Table 4. The contribution of plasma background emission to the Ag distribution was assessed by recording a sequence of images from a blank atomization of 10 µL of 1% HNO₃ under identical furnace temperature and plasma conditions. This sequence was then subtracted from the analyte sequence to yield the background-corrected analyte distribution. The effect of rf power on the distribution of Ag emission was ascertained using 30 W, 50 W and 70 W plasmas for which the dc bias on the centre electrode was maintained at 0 V.

3.3 RESULTS AND DISCUSSION

Optical resolution in the imaging system described in this study is obtained through the use of interference filters and, therefore, the spectral resolution that can be achieved (typically 10 nm) is poor by the standards of conventional atomic emission spectroscopy. Hence, a judicious matching of interference filter with spectral line is required and appropriate caution must be exercised in the interpretation of results. Wavelength traces of background structures formed in a Massmann-type FAPES atomizer using He as the plasma gas under conditions similar to those used in this work have been recorded by Sturgeon *et al.* [209]. They reveal that the bandpasses of the interference filters used in this work are sufficient to isolate predominantly only the molecular background spectral features desired (see Table 4), with the exception of the N₂ Second Positive System which also contains the 388.89 nm He I line and several prominent transitions of the CN Violet System. The He I line lies on the far wing of the bandpass of the interference filter used (380 ± 10 nm), with the result that transmission efficiency is poor (about 1%) and its contribution to the measured N₂ distribution is negligible. As well, CN emission would only be expected to contribute significantly to the N₂ distribution at elevated temperatures when the vapour pressure of carbon is sufficient to form a significant amount of CN. For the imaging of Ag emission transients, plasma background lines arising from the firing of a “blank” graphite tube were subtracted from the analyte distribution using the CCD imaging software, as described in the Experimental section. Obviously, this procedure would not compensate for the presence of any molecular analyte species contained within

the spectral bandpass of the interference filter used. It is generally accepted, however, that silver salts are reduced to metallic Ag on the graphite surface and atomization occurs from direct volatilization of the metal without the production of volatile intermediate molecular oxide species [226,227]. The 340 ± 10 nm filter used effectively isolates the Ag I 338.29 nm analysis line from other Ag atomic or Ag₂ transitions [106,224] and, although weak AgO bands occur at 349.34, 349.01, 348.77 and 348.42 nm [224], these lie on the far edge of the interference filter bandpass where the transmission efficiency is poor (~1%). If such species were formed, which is very unlikely under the conditions existing in the graphite furnace, they would not be detected.

3.3.1 Effect of the dc bias of the Centre Electrode on the Spatial Distribution of Helium and Plasma Background Gas Species

Figure 38 shows the spatial distribution of the He I 667.82 nm line across the central axis of the graphite tube obtained using a 50 W plasma, 0 V dc bias on the centre electrode and the tube wall at room temperature. The image in Fig. 38 (a) is a false-coloured representation of the actual CCD image where white represents the highest intensity and black represents the lowest intensity. The three-dimensional plots of Fig. 38 (b) are graphs of pixel intensity over the cross-section of the graphite tube. As a result of the depth-of-field of the optics, all intensities are integrated along the length of the graphite tube so no longitudinal information can be obtained. From Fig. 38 (a), it is evident that there is an intense region of plasma surrounding the centre electrode along with a diffuse

Figure 38. Cross-sectional distribution of the He I 667.82 nm line intensity obtained with the graphite tube at room temperature, a forward rf power of 50 W and a 0 V dc bias imposed on the centre electrode: (a) false-coloured image and (b) three-dimensional response surface.

outer ring close to the tube walls, with comparatively little emission in the intermediate region. The intensity of the plasma surrounding the centre electrode is approximately 20-fold greater than that of the outer ring. The outer ring does not terminate at the walls, but is recessed from them by a "dark space" of roughly $90\text{ }\mu\text{m}$ thickness. This estimate was made by heating the graphite tube to approximately 2000°C in the absence of a plasma and recording the incandescent image of the tube wall through the same interference filter used to isolate the He I 667.82 nm line. This image was then added (using the Image200 software) to an image obtained for the He plasma with the tube at room temperature. A gap between the thermal emission image of the inner tube wall and the terminus of the outer plasma ring was evident; its magnitude was estimated from the image display on the computer screen, given that the internal diameter of the tube is 6 mm .

One may argue that the outer ring occurs as a result of reflection of light off the tube wall from the plasma surrounding the centre electrode, or that it may arise from photoelectrons ejected from the tube wall interacting with the plasma support gas. Subsequent experiments have shown that the second plasma exists as a consequence of the reversal of polarity of the rf field between the centre electrode and the tube wall. In a study of an atmospheric pressure rf glow discharge formed between two parallel-plate copper electrodes of equal area, Hotz [228] found that the (negative) glow shifted position and was associated solely with the electrode which acted as the cathode during a given half-cycle. Because of the rapidity of this process with respect to the integration time of the human eye, the glow appeared to be simultaneously located at both electrodes [228]. This situation also occurs with the co-axial cylindrical electrode geometry employed in

FAPES. The weaker intensity of the outer ring plasma is a consequence of the 40-fold larger surface area of the outer electrode (6 mm o.d. graphite tube) relative to the centre electrode (1 mm o.d.). Experiments were undertaken to determine the effects of dc bias on the centre electrode on the structure of the plasma. A constant forward power of 50 W was maintained. The effect of a change in the dc bias of the centre electrode on the plasma is also of practical interest from an analytical standpoint since the dc self-bias of the centre electrode has been shown to change significantly during the course of an emission transient, momentarily attaining values of approximately -120 V at elevated temperature from an initial (room temperature) potential of about -10 V [197].

Figure 39 represents the images and corresponding three-dimensional intensity plots of emission from the He I 667.82 nm line in a graphite tube as the dc bias of the centre electrode is made increasingly negative. The distribution for the -12 V bias case is of interest in that it is most representative of a self-bias FAPES system operating with the tube wall at room temperature. As the dc bias of the centre electrode is made more negative there is a small but significant increase in the intensity of the plasma surrounding it. Although not particularly evident from the 2-D distributions, this increase is clearly revealed in the 3-D plots when they are compared to the 0 V bias case [Fig 38. (b)]. The outer ring intensity decreases slightly as the dc bias is made more negative; unfortunately, the large scale used in this series of figures precludes a clear representation of this condition. These intensity changes would support the belief that the outer ring does not result from reflection or excitation by emitted photoelectrons. Were this the case, an increase in the intensity of the centre plasma (and, hence, an increase in the flux of

Figure 39. Effect of increasing negative dc bias potential of the centre electrode on the cross-sectional distribution of intensity from the He I 667.82 nm line. The rf power was 50 W and the graphite tube was at room temperature. (a) False-coloured images at (i) -12, (ii) -47, (iii) -83 V dc bias; (b) three-dimensional response surface at (i) -12, (ii) -47, (iii) -83 V dc bias.

photons to the tube wall) would also bring about an increase in the intensity of the outer ring. The observed increase in the centre electrode plasma with increasing negative dc bias can be explained by considering that a larger negative dc bias on the centre electrode implies that it behaves as the cathode for a greater period of time during a given half-cycle [51].

Figure 40 illustrates the effects of increasing positive dc bias on the centre electrode. In general, with increasing positive bias the intensity of the centre electrode plasma decreases and there is enhanced emission in the region between the centre electrode and the tube wall. Most significantly, however, plasma intensity at the tube wall increases as positive bias is increased to +83 V. These effects can be explained by considering that a positive dc bias applied to the centre electrode will cause the counter-electrode (graphite tube) to behave as a cathode for a greater period of time during a given half cycle, such that the plasma will be enhanced near its surface. The increase in intensity of this plasma coupled with the decrease in intensity of the centre electrode plasma with increasing positive bias are consistent with the above hypothesis. At a low positive bias of 12 V [Fig. 40 (a) (i)], two regions of plasma are established at the wall, possibly reflecting the presence of a “negative glow” and a “cathode glow” at the wall. It may be that a “negative glow” and a “cathode glow” exist at the centre electrode, but are not resolved from one another owing to the intensity of the centre electrode plasma and the small surface area of the centre electrode. Because of the larger surface area of the tube wall relative to the centre electrode, these regions then become resolved at the wall as the polarity shifts and the field reverses. As the dc bias is increased above +25 V, however, the wall plasma

Figure 40. Effect of increasing positive dc bias potential of the centre electrode on the cross-sectional distribution of intensity from the He I 667.82 nm line. The rf power was 50 W and the graphite tube was at room temperature. (a) False-coloured images at (i) +12, (ii) +35, (iii) +83 V dc bias; (b) three-dimensional response surface at (i) +12, (ii) +35, (iii) +83 V dc bias.

merges into a single glow, most probably due to increases in the intensities of both the “cathode glow” and “negative glow”.

To further investigate the source of the outer ring plasma, biasing experiments were repeated using a pyrolytic boron nitride tube and a Macor tube. Representative examples of the distributions obtained with these tubes are provided in Figure 41. Although the intensity of the centre plasma in the boron nitride tube [Fig. 41 (a)-(b)] was found to be of similar magnitude to that obtained for a graphite tube, the outer ring plasma was more intense (~4-fold). This suggests a greater contribution of electrons to the ring plasma, possibly as a consequence of a lower work function for secondary electron emission from this surface [197]. For the Macor tube, the intensities of both the centre electrode and ring plasmas were about half of that of the corresponding plasmas in a graphite tube [Fig. 41 (c)-(d)]. As well, the plasma intensity appears to be more uniformly distributed over the cross-section of the tube. Since the Macor tube is an insulating material, the corresponding counter electrode for this system effectively becomes the furnace housing, some further distance beyond the tube. This decreases the electric field gradient and, by consequence, the intensity of both plasmas. In contrast to a graphite tube, the spatial distribution of the plasma formed in a boron nitride or Macor tube remains largely unchanged by alteration of the dc bias of the centre electrode. No “cathode glow” at the walls is observed with the application of a positive bias voltage and the relative intensities of the centre electrode plasma and the outer ring remain essentially the same regardless of the applied dc bias. The marginal change associated in plasma structure with changes in dc bias for these insulating materials can be explained as follows. Because an insulating

Figure 41. The effect of tube material on the distribution of He I 667.82 nm line intensity.

The forward rf power was 50 W and the tube wall was at room temperature. (a) Boron nitride-coated tube, -50 V dc bias; (b) boron nitride-coated tube, +50 V dc bias; (c) Macor tube, -37 V dc bias; and (d) Macor tube, +12 V dc bias.

surface is incapable of conducting a charge, its potential will float to the potential of the centre electrode and, thus, the changes noted for the graphite tube will not be observed for such surfaces, *i.e.*, there will be no change in the time a given electrode acts as the cathode during a given half-cycle.

Although L'vov platforms have been used in FAPES without any analytical difficulties [210], the effect of the platform on the distribution of the centre electrode and outer ring plasmas has not been studied. For this purpose, a 2.5-cm long graphite strip and a 2.8-cm Macor strip were placed inside graphite, boron nitride and Macor tubes. Macor and BN were selected to provide insulating surfaces which, unlike graphite, would not readily take the potential of the tube wall. Figure 42 shows the images obtained with a 50 W, 0 V bias plasma for a graphite, boron nitride and Macor tube. As images of the boron nitride and Macor tubes were acquired using different camera exposure conditions, absolute intensity comparisons for these systems cannot be made. For all tube materials there is an absence of the outer plasma ring beneath the strip. The outer ring instead terminates at the strip and extends around the central plasma. Although there is weak emission beneath the strip, no distinct plasma structure is evident. Figure 42 (a) shows the results obtained with a graphite tube and graphite strip whereas, in Fig. 42 (b), results for a Macor strip are illustrated. For the graphite strip, there is enhanced emission between the electrode and the strip, while the intensity of the outer ring plasma is similar to that obtained in a graphite tube in the absence of a strip (~ 100). The presence of the Macor strip in the graphite tube has the effect of increasing the overall intensity of the outer ring plasma (to ~ 500) while decreasing the emission between the electrode and the

Figure 42. False-coloured images illustrating the effect of a strip on the distribution of the He I 667.82 nm line intensity in various tube and strip materials. The forward rf power was 50 W, the dc bias of the centre electrode was 0 V, and the tube wall was at room temperature. (a) graphite tube and graphite strip; (b) graphite tube and Macor strip; (c) boron nitride-coated tube and Macor strip; and, (d) Macor tube and Macor strip.

strip. The enhanced emission between the electrode and the graphite strip is likely a consequence of the enhanced field gradient as the electrode-tube wall distance is decreased. No difference in the characteristics of graphite or Macor strips in boron nitride or Macor tubes was noted, presumably because the potential of these insulating tube materials float with respect to the centre electrode potential, as noted earlier. Macor strips inserted into boron nitride or Macor tubes [Fig. 42 (c)-(d)] exhibit the same general distribution as was observed for the graphite tube/Macor strip system in that the outer plasma ring terminates at the strip and then tends to deflect around the centre electrode.

Figure 43 shows the false coloured images obtained in a graphite tube for background molecular species CO^+ , N_2 , NO and OH at 50 W power with a 0 V dc bias on the centre electrode and the graphite tube wall at room temperature. Corresponding three-dimensional response surfaces for these images are given in Figure 44. No relative intensity intercomparisons can be made for these images in Fig. 43 as a consequence of the different exposure times used. In general, the distributions of these species are analogous to those obtained for He and their response to changes in applied dc bias are also similar. However, the ratio of the centre electrode plasma intensity to the outer ring plasma intensity differs for the different species as does the extent of emission between the centre electrode and the tube wall. The distribution of CO^+ [Fig. 43 (a)] is most similar to that observed for He and is also in good agreement with the distribution measured by Hettipathirana and Blades [204]. Nitrogen, NO and OH exhibit progressively increasing radial emission intensity and progressively decreasing centre electrode plasma intensities relative to the intensities of the outer ring. A similar broad distribution for OH has also

Figure 43. False-coloured images of the spatial distribution of polyatomic background species in FAPES (using a graphite tube). The spatial features isolated and the interference filters used are listed in Table 4. The forward rf power was 50 W, the dc bias of the centre electrode was 0 V and the tube wall was at room temperature. (a) CO^+ , (b) N_2^+ , (c) NO, and (d) OH.

Figure 44. Three-dimensional response surfaces of the spatial distribution of polyatomic background species in FAPES (using a graphite tube). The spatial features isolated and the interference filters used are listed in Table 4. The forward rf power was 50 W, the dc bias of the centre electrode was 0 V and the tube wall was at room temperature. (a) CO^+ , (b) N_2 , (c) NO , and (d) OH .

been noted by Hettipathirana and Blades [204]. These emission patterns follow the relative excitation energies for these species, *i.e.*, OH (4.05 eV), NO (5.45 eV), N₂ (11.05 eV), CO⁺ (19.39 eV) [218].

3.3.2 Ingress of Atmospheric Components into the FAPES Plasma

The ingress of components of atmospheric air into graphite furnace atomizers has been the subject of considerable investigation [229-232]. Sturgeon *et al.* [218] have shown that most of the nitrogen-containing background species in a He FAPES plasma can be eliminated by using an enclosed integrated contact cuvette (ICC) furnace. This would suggest that the ingress of components of the atmospheric air into “open” Massmann-type FAPES atomizers is a significant source of nitrogen- and oxygen- containing molecular background species. In view of this, attempts were made to observe the ingress of nitrogen by imaging the Nitrogen Second Positive System (see Table 4). Figure 45 presents a selection of such images, obtained at 1 s intervals, as a dry, unloaded furnace was ramped from room temperature to 2000°C at a rate of 1250°C s⁻¹. Figure 45 (a) shows the N₂ distribution at the onset of the ramp which can be regarded as being at essentially room temperature. This image is typical of that presented in Fig. 43 (b) and exhibits no unusual structure. No significant structural features are observed until 4 s into the ramp when the graphite tube first reaches its steady-state temperature of 2000°C. At this point, a “plume” appears, extending from the dosing hole down to the bottom of the graphite tube, radially filling much of the tube volume. The emission intensity at the

Figure 45. False-coloured images illustrating ingress of atmospheric nitrogen into a graphite tube. The forward rf power was 50 W, the dc bias of the centre electrode was 0 V. See Table 4 for the interference filter used and the spectral features isolated. (a) time = 0 s; (b) time = 4 s; (c) time = 10 s.

dosing hole is approximately twice that near the tube bottom. This distribution remains essentially unchanged in structure over the next 6 s, although its overall intensity increases, as is evident from Fig. 45 (c). It is noteworthy that the distribution resulting from ingress of air obtained experimentally in this study is, in general form, quite similar to the theoretical distribution calculated by Gilmutdinov *et al.* [232] for the ingress of oxygen into graphite tube atomizers.

Although images of N₂ ingress were obtained at elevated temperatures, attempts to reproduce this structure at room temperature were unsuccessful. Increasing the forward power to 80 W or altering the dc bias from +25 to -38 V to change the plasma properties had no effect, even in the absence of an external purge gas flow and with a low internal plasma gas flow rate (~120 mL min⁻¹). It was found that a minimum tube wall temperature of 1900°C was required (80 W, 0 V bias plasma) for the “plume” to be observed. These results are somewhat surprising in light of the findings of Sturgeon and Falk [231] who directly showed that the ingress of atmospheric O₂ into a Massmann-type graphite furnace atomizer at room temperature occurred even in the presence of both internal and external purge gas flows. A likely explanation for the results of this work is that the He FAPES plasma is not sufficiently energetic with the tube wall at room temperature to allow the ingress of N₂ to be imaged. Several strong bands of the Violet System of CN fall within the bandpass of the interference filter used to isolate the N₂ Second Positive System and its relatively low excitation energy (3.27 eV; see Table 4) make its excitation likely. As the furnace temperature rises, the internal partial pressure of carbon increases such that N₂ entering through the sample injection hole readily reacts

to form CN which then becomes excited in the plasma. This would account for the fact that the plume is observed only at elevated furnace temperatures ($\geq 1900^{\circ}\text{C}$). This is in accord with the results of Ohlsson and Frech [233] who measured $p\text{CN}$ values beginning at 2300 K. It should also be noted that the results described above were obtained with a "worn" electrode whose length had been eroded by He^+ sputtering and volatilization of carbon during repeated heating cycles. Attempts to reproduce the nitrogen ingress images with a fresh electrode traversing the entire length of the tube yielded irreproducible results. This is explicable in light of previous work [203] which has shown that excitation temperatures in FAPES increase with decreasing electrode length; thus a short electrode (terminating a few mm beyond the sample injection hole) is required to provide an elevated partial pressure of carbon (for CN formation) which derives from a worn electrode surface. Additional factors may also come into play to account for formation of the plume. The fact that a minimum tube wall temperature of 1900°C is required before nitrogen ingress is observed may suggest that thermionic electrons emitted at this temperature may play a role in enhancing the excitation capability of the plasma. Additionally, the plume is only observed after the graphite tube has reached a steady-state temperature, possibly because there would be a concomitant expulsion of the internal plasma gas out of the dosing hole in the initial stages of the heating ramp which would serve as an added barrier to the influx of nitrogen. As the tube reaches its steady-state temperature and the expulsion of the internal gas ceases, the barrier to the influx of nitrogen is removed, causing the concentration of nitrogen in the atomizer to increase sufficiently to enable the plume to be observed in the (more energetic) plasma.

3.3.3 *Distribution of Excited-State Silver Atoms during an Atomization Transient*

Figures 46 to 48 display sequences of images obtained for 40 ng Ag atomized from the tube wall into 30 W, 50 W and 70 W plasmas (0 V bias), respectively. For the 30 W case (Fig. 46), two distinct emission events are evident. At 0.05 - 0.15 s there is weak Ag emission near the centre electrode, probably as a result of violent shattering of the AgNO₃ crystal lattice on heating with transfer of analyte onto the cooler centre electrode, as the tube temperature is too low at this time to promote atomization of Ag. Weak Ag emission at the wall, where the sample was originally deposited, also occurs. Subsequently (0.20 - 0.25 s) enhanced Ag emission originates at the tube wall as atomic Ag is transferred from the wall to the cooler centre electrode. The extremely weak Ag emission noted in images 0.35 - 0.50 s and localized at the centre electrode suggests that the electrode has not yet reached a temperature sufficient to promote release of the condensed Ag. Release of Ag from the centre electrode begins to occur at 0.55 s and Ag expands to fill the entire tube volume at 0.60 - 0.75 s, after which dissipation begins. Imai and Sturgeon [215] have reported the temperature of the centre electrode to be 450 K for a 30 W plasma and found that plasma-assisted heating of the tube wall is essentially negligible for forward rf powers of 30 W and less. Therefore, the early condensation/transfer of Ag onto the electrode surface seen between 0.05 - 0.50 s appears reasonable, as does the subsequent volatilization of Ag from the centre electrode. For a 50 W plasma, two distinct emission events are also observed (Fig. 47). Silver emission occurs early in time exclusively at the wall (0.10 s) and then in the tube volume as Ag

Figure 46. False-coloured images for 40 ng Ag atomized from the tube wall for a forward rf power 30 W, with 0 V dc bias imposed on the centre electrode. The observed emission is from the Ag I 338.29 nm resonance line.

Figure 47. False-coloured images for 40 ng Ag atomized from the tube wall for a forward rf power 50 W, with 0 V dc bias imposed on the centre electrode. The emission observed is from the Ag I 338.29 nm resonance line.

Figure 48. False-coloured images for 40 ng Ag atomized from the tube wall for a forward rf power 70 W, with 0 V dc bias imposed on the centre electrode. The emission observed is from the Ag I 338.29 nm resonance line.

atomic vapour transfers from the wall to the centre electrode (0.15 - 0.30 s). No Ag emission is observed at 0.35 s - 0.40 s due to insufficient heat at the electrode; Ag condensed on the electrode is subsequently released at 0.45 s and beyond. Unlike atomization into a 30 W plasma (Fig. 46), no weak Ag emission was observed at the electrode either early or late in the transient, most probably as a consequence of increased plasma-induced heating of the electrode at 50 W (600 K vs. 450 K [215]). In contrast to the 50 and 30 W cases, atomization into a 70 W plasma yields only one distinct emission event (Figure 48). FAPES plasmas operated at forward rf powers of greater than 50 W have been found to exhibit substantial plasma-induced heating of both the tube wall and the centre electrode [215], with the result that double peaks associated with analyte condensation and re-volatilization processes are reduced or removed entirely. This is borne out by the sequence of images in Fig. 48 which show Ag emission beginning directly beneath the centre electrode (0.05 s) rapidly filling the tube volume (0.20 - 0.55 s) and then dissipating. Similar condensation-revaporization effects have been noted for Cd and Cr in the low pressure HA-FANES system [35,38].

3.4 CONCLUSIONS

Two plasmas exist in the FAPES source, lending it substantial radial inhomogeneity. In addition to an intense plasma surrounding the centre electrode, there exists a diffuse outer plasma near the tube wall. The spatial distribution of the plasma formed in a graphite tube is significantly influenced by the dc bias of the centre electrode.

The ingress of atmospheric nitrogen can be followed by observation of CN emission at elevated temperature when atmospheric N_2 combines with carbon volatilized from the graphite tube. Images obtained for the atomization of Ag into plasmas operated at forward rf powers of 30 W, 50 W and 70 W illustrate that, while condensation and re-vaporization from the centre electrode are significant at the lower plasma powers, plasma-induced heating of the centre electrode and the tube wall at 70 W is sufficient to prevent the centre electrode from acting as a condensation site.

CHAPTER 4

THE EFFECT OF EASILY-IONIZED ELEMENTS AND EXCITATION CONDITIONS ON THE SPATIAL DISTRIBUTION OF ANALYTES IN THE FURNACE ATOMIZATION PLASMA EMISSION SPECTROMETRY SOURCE

4.1 INTRODUCTION

One of the primary motivating factors behind the development of combined analytical sources such as Furnace Atomization Plasma Emission Spectrometry (FAPES) is the potential to decouple atomization and excitation phenomena, thereby potentially minimizing matrix effects. Additionally, the collision-rich environment provided by the plasma was hoped to be sufficiently robust to dissociate or be insensitive to any matrix components that were co-volatilized with the analyte. Unfortunately, as was noted in Chapter 3, complete decoupling of excitation and atomization processes in FAPES cannot be realized as the heat of the graphite tube influences the production of thermionic electrons which can alter plasma processes. Additionally, the power influences the temperature of the centre electrode which, in turn, determines the extent to which it acts as a site for primary condensation and re-desorption of analytes. This intimate interaction between thermal and non-thermal effects manifests itself, to varying degrees, in all the FANES sources discussed in this thesis. Furthermore, the fact that studies on “real” samples conducted with combined “non-thermal” excitation sources have thus far employed the method of standard additions [210] suggests that matrix effects play a significant role in altering the excitation characteristics of these plasmas.

4.1.1 Easily Ionized Elements in FAPES and FANES Sources

Possibly the most common type of interference from the sample matrix reported in analytical plasmas is that resulting from the presence of Group I and II elements, commonly referred to as Easily Ionized Elements (EIEs). Like emitted thermoelectrons, EIEs will alter the discharge potential, possibly producing substantial voltage drops which attenuate the energetics of the discharge, thus decreasing analyte excitation. Less common, but also possible, are enhancements in analyte emission as the result of the EIE acting as a "buffer" for analyte ionization. This latter effect is most likely to be prevalent in high-energy ionizing plasmas.

Falk [22] has developed general equations for analyte excitation and matrix effects in analytical plasmas. Assuming electron-impact excitation, the excitation frequency per unit time and volume (k_{ex}) is given by:

$$k_{ex} = n_a n_e \int_0^\infty v_e f_e(E_e) A_{ex}(E_e) dE_e \quad (4.1)$$

where n_a is the atom density (cm^{-3}), n_e is the electron density (cm^{-3}), v_e is the electron velocity (cm s^{-1}), E_e is the electron energy (eV), $f_e(E_e)$ is the electron energy distribution (eV^{-1}) and $A_{ex}(E_e)$ is the excitation cross-section (cm^2). The excitation rate must be balanced by the collisional de-excitation rate, which will be altered by an EIE. For a two-level system, the ratio of excited to ground-state atoms can be written as follows:

$$\frac{n^*}{n_0} = \frac{CE}{CD + RD} \quad (4.2)$$

where CE, CD and RD are the rates for collisional excitation, collisional de-excitation and radiative de-excitation, respectively. The maximum concentration of matrix species relative to the discharge gas in the graphite furnace is:

$$c_{rel,m} = \frac{\epsilon c_m V_s N_A}{n_c M V_a} \quad (4.3)$$

where ϵ is the atomizer efficiency, c_m is the sample matrix concentration, (g cm^{-3}), V_s is the sample volume, N_A is Avogadro's number, n_c is the carrier gas density, M is the molar mass and V_a is the atomizer volume. Assuming that the photons from excited atoms leave the plasma, the power loss (P_{ex}) by this process is:

$$P_{ex} = k_{ex} r_{dp} E_{ph} V_{so} \quad (4.4)$$

where k_{ex} is the excitation frequency defined in Equation (4.1), $r_{dp} = \text{RD}/(\text{CD} + \text{RD})$, E_{ph} is the photon energy and V_{so} is the source volume. Equations (4.1 - 4.4) can be used to calculate the matrix concentration of any species in the plasma which would dissipate a given fraction of the input power *via* excitation losses. Falk [22] has calculated that the maximum tolerable Na concentration which would bring about a 10 % loss of discharge power is 0.005 % for FANES, 0.01 % for FAPES and 0.05 % for inductively-coupled plasma (ICP) emission sources. These calculations clearly show that matrix effects can be severe for combined “non-thermal” excitation sources even at relatively low matrix concentrations, with the severity of the interference being dependent upon the degree of temporal overlap between the analyte and interferent.

Falk found that the emission from Cu was suppressed by 20 % in the presence of 2 μg of NaCl in HC-FANES [22]. For HA-FANES, Riby and Harnly [38] found that

significant perturbations in discharge voltage occurred in He at 400 torr and 130 mA for only 0.25 μg NaCl. Operation at elevated pressure (600 torr) and higher current (200 mA) was found to significantly reduce voltage perturbations in the presence of up to 2.5 μg NaCl. For FAPES, Smith *et al.* [208] found that emission from Ag was initially enhanced in the presence of NaCl, but that it decreased beyond 1.2 μg of the salt. The initial enhancement was ascribed to suppression of Ag ionization by NaCl ("buffering" effect), whereas the intensity decrease at higher salt masses was believed to result from a decrease in plasma excitation characteristics. Subsequently, Hettipathirana and Blades [214] found that even small masses (162 ng) of NaCl and NaNO₃ were sufficient to alter plasma excitation characteristics and the extent of molecular dissociation for Pb and Ag for a FAPES source operated at input powers of 14 - 40 W and a low heating rate of 360 K s⁻¹. Significant suppression was observed for Pb emission signals in the presence of 1 - 3 μg NaCl, although high input powers could decrease the extent of the suppression. Using a commercial ICC FAPES source, Gilchrist and Liang [194] found that the emission intensity of Tl could be suppressed by the presence of only 0.08 μg NaCl.

Easily-ionized elements may affect analyte excitation in FAPES by various mechanisms. Analyte emission intensity may be decreased by expulsion loss of analyte from the excitation/observation volume as the result of co-vaporization with the EIE matrix; chemical interference due to analyte molecule formation; decreased plasma power available for analyte excitation as the result of photon emission by excited EIE matrix species; de-tuning, or loss of plasma power coupling efficiency because of changes in the load impedance of the plasma brought about by the EIE; and alterations in the self-bias

voltage resulting from changes in electron density in the presence of the EIE. Enhancements in analyte emission intensity in the presence of EIEs may be brought about by an increased gas density of the diffusion medium as a significant amount of He is replaced by matrix vapour; shifts in analyte ionization equilibrium due to ionization of matrix elements; and decreased gas kinetic temperature accompanying the EIE power dissipation mechanisms described above. Finally, analyte excitation may either be enhanced or decreased by an alteration of the electron energy distribution function (EEDF, or $f_e(E_e)$ in Equation 4.1) due to the release of electrons from the EIE through ionization, or by attenuation of plasma electron energy from excitation or molecular dissociation of matrix species, depending on the analyte excitation energy relative to the original and altered EEDF. Imai and Sturgeon [216] have shown that depletion of analyte excitation in the presence of EIEs is most likely due to radiative power losses from excitation of EIE matrix species and alterations in the EEDF, rather than by classical analyte molecule formation, gas-phase expulsion and de-tuning of the plasma.

Chemical modification [211,212] and the Stabilized Temperature Platform Furnace (STPF) concept [211] have been successfully employed in FAPES. Preatomization losses of P as PO were suppressed with Pd modifier [212] and platform atomization in the presence of Pd dramatically decreased the NaCl interference on Pb, enabling ~75 % recovery of the metal in the presence of 24 μg NaCl [211]. Chemical modification and platform technology, however, cannot be applied in FAPES with the same latitude that it is used in GFAAS. The mass of any modifier must be minimized, since large masses will cause the plasma to arc to the sample deposition site. Although this situation can be

alleviated somewhat through the use of a platform, in Massmann furnaces these place limitations on the determination of involatile elements, thus compromising the simultaneous multielement analysis inherent to FAPES. Additionally, since FAPES is an emission technique, the possibility of spectral line overlap between analytes and modifier components may limit the applicability of certain modifiers for particular analytes. The ultimate aim of FAPES is simultaneous multielement analysis for analytes with widely varying thermal properties using as similar analytical conditions as possible. Restrictions on the use of modifiers, platforms and elaborate thermal pre-treatment programs may result.

All prior investigations into the effect of easily-ionized elements on FANES and FAPES response have sampled one region of the plasma exclusively (typically immediate to the centre electrode). Studies outlined in Chapter 3 have shown that FAPES is a highly non-homogenous discharge with regions of emission that vary widely in intensity and that the spatial structure of the plasma is strongly affected by the dc bias of the centre electrode. Sturgeon *et al.* [197] found that control of the dc bias of the centre electrode decreased fluctuations in excitation temperatures during the course of an atomization transient in clean matrices. Since EIEs alter excitation temperatures in non-thermal excitation sources [38], bias control may afford a more robust plasma to minimize the effects of the presence of EIEs. Several studies of ICP discharges [234-236] have revealed that EIE effects are strongly spatially-dependent. Since spatial effects are observed for EIEs in such comparatively symmetric plasmas, it is not unreasonable to assume that the spatial response of analytes to the introduction of EIEs would be even more pronounced

for FAPES. The aim of this chapter is to (a) to determine whether changes in excitation conditions of the plasma (primarily, as determined by the dc bias of the centre electrode) lead to significant changes in the spatial distribution of analytes atomized into the plasma; (b) to determine whether the introduction of EIEs into the plasma significantly alters the spatial distribution of the plasma and (c) to determine whether control of the dc bias of the centre electrode changes excitation conditions of the plasma sufficiently to ameliorate effects of EIEs. In this respect, NaCl, NaNO₃, CsCl and Fe were selected as matrix species and Ag and Cu, which represent elements of different volatilities, were selected as test elements as they both have temporal overlaps with the above interferents.

4.2 EXPERIMENTAL

4.2.1 Reagents

The discharge gas used was liquid chromatographic grade helium (Air Products Canada Ltd., Nepean, ON, Canada), first passed through a molecular sieve and then the graphite furnace *via* the internal purge gas port at a flow rate of 200 mL min⁻¹. High purity Ar (99.995 %; Canadian Oxygen, Ltd., Mississauga, ON, Canada) served as the external purge gas and was maintained at a flow rate of 1 L min⁻¹. Stock solutions (1,000 or 10,000 µg ml⁻¹) were prepared from dissolution of the high-purity metals (Cu, Ag and Fe) or their salts (NaCl, NaNO₃ and CsCl). Working standards were prepared fresh daily by dilution of the stocks with high-purity (18.3 MΩ cm resistivity) distilled, de-ionized

water and acidified to 1 % (v/v) with HNO_3 (Ultrex grade; J.T. Baker Canada, Toronto, ON, Canada).

4.2.2 Instrumentation

A detailed description of the optical imaging spectrometer, atomizer workhead, rf generator and dc bias control unit used has already been provided in Chapter 3. For the work described in this chapter, a Perkin-Elmer (Norwalk, CT, USA) model HGA-500 graphite furnace power supply/controller was used in place of the HGA-76B power supply previously employed. The HGA-500 supply has maximum power heating rate of $\sim 2000\text{ }^\circ\text{C s}^{-1}$, compared to the $\sim 1250\text{ }^\circ\text{C s}^{-1}$ achievable with the HGA-76B controller. This is advantageous in terms of analytical sensitivity. Furthermore, the HGA-500 is a microprocessor-driven unit, permitting acquisition of the emission transient in increments of 1 s before or after the actual commencement of the high-temperature volatilization step. Because time-resolved imaging of analyte emission transients was desired, the charge-coupled device (CCD) camera (Photometrics, Ltd., Tucson, AZ, USA) used to image the central cross-section of the graphite furnace interior was operated in frame-transfer mode. The CCD chip was binned 4×4 to obtain a nominal image array size of 62×62 . Such conditions yielded an acquisition rate of 50 ms per image. To obtain the greater spatial resolution required for imaging He plasma species the full resolution of the CCD chip was used (*i.e.*, 1×1 binning), whereas all other image acquisition steps remained unchanged. As a consequence of the larger image array size that is produced when binning is not used,

the time required for the CCD system to read out the contents of the image array increased. Thus, for imaging of He and plasma gas species the acquisition rate was 400 ms per image.

Optical resolution in the imaging system was again achieved through the use of interference filters. Although this results in a bandpass of 10 nm or more, the CCD allows the background to be stored and subtracted from the analytical run for accurate recording of analytical transients. The spectral transitions monitored and interference filters used in this chapter are listed in Table 5. The wide bandpass of the system means that, in the case of Cu and Ca II, the images obtained were composites of emission from at least two spectral transitions. Imaging of Ag in the presence and absence of NaCl and NaNO₃ was done using a 330 nm central maximum (10 nm FWHM) interference filter to isolate the Ag I 328.07 nm resonance line. Although Na I transitions at 330.23 nm and 330.30 nm are passed by this filter, emission from Na I was not detected by the CCD as a consequence of its insensitivity *vis à vis* a photomultiplier tube. Before recording emission images from analytes in the presence of interfering species, images from the interfering species alone were recorded. In all cases, no emission from the interfering species was detected.

4.2.3 Procedures

Images of FAPES transients were obtained as follows. Solutions (5 - 40 μ L) of the analyte and/or interferent were manually pipetted into the graphite furnace using fixed-

Table 5. Spectral features monitored and interference filters used for detection of excited-state silver, copper, helium, ionic calcium and cesium.

Spectral Transition	Excitation Energy (eV)	Central Wavelength and FWHM of Interference filter (nm)
Ag I 328.33 nm	3.45	330 ; 10
Cu I 324.75 nm	3.82	326 ; 10
Cu I 327.40 nm	3.78	326 ; 10
He I 388.86 nm	23.00	390 ; 10
Ca II 393.37 nm	9.26	395 ; 10
Ca II 396.85 nm	9.24	395 ; 10
Cs I 852.11 nm	1.45	850; 25

volume Eppendorf pipettes. The sample was then dried at 120 °C for 60 s and “charred” at 400 °C for 60 s. Temperature readings refer to those read directly from the HGA-500 power supply. The lengthy dry and charring times were used to minimize the effect of entrained water vapour, which has been shown to have deleterious effects on similar “non-thermal” discharges [80,237]. The graphite tube was then allowed to cool to room temperature, after which the plasma was ignited. The graphite tube temperature was then ramped to 400 °C for 5 s (to function as a plasma “pre-stabilization period”). Using maximum power heating conditions, atomization at the desired temperature was then initiated for 5 s. For Cu and Ca II, this was set to 2600 °C, whereas for Ag this was set to 1700 °C. Cesium and sodium were atomized at both 2600 °C and 1700 °C to reflect the relative temporal overlap of these elements for Cu, Ca II and Ag analytes. In the case of an analyte in a clean matrix, the background contribution to the emission intensity was assessed by atomizing a blank consisting of 1 % HNO₃ under the same conditions as the analyte. In the case of analyte/interferent combinations, the blank consisted of the interferent alone in 1 % HNO₃, which was again atomized under conditions identical to that of the analyte. Emission from He I and plasma background species was imaged under transient conditions by heating an empty graphite tube from 400 °C to 2600 °C. The blank for such a system consisted of heating the empty graphite tube in the absence of a plasma. In all cases, the blank series of distributions was subtracted from that of the analyte to yield background-corrected analyte distributions. In most cases, rf forward power was applied at 50 W (as read on the port of the rf tuner), although for other experiments the rf power was varied from a minimum of 20 W to a maximum of 100 W.

Reflected powers were tuned to ≤ 1 W in all cases ("room temperature" value). The dc bias on the centre electrode was varied from -50 V to +40 V using a series of 12-V motorcycle batteries, as described in Chapter 3.

4.3 RESULTS AND DISCUSSION

4.3.1 Effect of dc bias on the Spatial Distribution of Helium Plasma Gas Species during an Atomization Transient

Before obtaining images of the spatial response of analyte transients to the presence of EIEs, it is first necessary to determine if any changes in the spatial response of the plasma and analytes occur in "clean" matrices during an atomization transient. In particular, it is important to obtain the images for the spatial distribution of He I, as this will serve as a first-approximation "template" of plasma excitation against which all observed analyte emission is convoluted. There is no practical way of masking the intense blackbody radiation from the heated tube walls using the imaging system. At long wavelengths and high temperatures blackbody emission overwhelms the He I signal, giving the illusion that the plasma has "collapsed". Thus, imaging of He I under high temperature conditions must be performed in the ultraviolet to minimize blackbody radiation. This requirement restricts He I imaging to the 388.86 nm line, which is unfortunate because it is spectrally isolated in the current imaging system only by a 10 nm FWHM, 390 nm central maximum interference filter. Studies by Sturgeon *et al.* [209] and Hettipathirana and Blades [204] have revealed that several strong nitrogen bands,

specifically those of the N_2 Second Positive system and the N_2^+ First Negative system, are excited in the FAPES discharge in the wavelength region of approximately 385 - 395 nm. Additionally, formation of CN Violet system bands in this wavelength region from entrained atmospheric air reacting with volatilized carbon, as illustrated in Chapter 3, cannot be ignored. Because the Massmann FAPES system used in this study operates in an "open" air environment, it is not possible to remove or diminish the contribution of the nitrogenous background species, making unambiguous determination of He I emission structure at high temperature impossible. Nevertheless, the spatial distribution of N_2 species in the FAPES source has been shown (Chapter 3) to be very similar to that of He. Furthermore, although mechanisms of excitation of the plasma gas species may be different, it is reasonable to assume that all plasma excitation mechanisms are ultimately powered by electrons [22,109] so that acquisition of the spatial distribution of plasma gas species should still provide a good approximation of the He excitation "template".

False-coloured images (where white represents the highest intensity and black the lowest) obtained for the He I 388.86 nm line in a dry, unloaded furnace appear in Figure 49. A forward rf power of 50 W was applied and the centre electrode was allowed to self-bias while the tube wall temperature was ramped to 2600 °C using maximum power heating. Under such conditions the dc self-bias of the centre electrode exhibits its greatest change from -10 V to -125 V (as illustrated in Figure 35, Chapter 3) and it is in this "free-running" mode that FAPES sources are most commonly operated. Before progressing to a discussion of the image analysis it must be mentioned that each image was scaled for optimal viewing and, hence, no absolute intensity intercomparisons can be drawn from the

Figure 49. False-coloured images for plasma gas species, including He I, N_2 , N_2^+ and CN gathered using a 390 nm peak maximum, 10 nm FWHM interference filter obtained for a blank tube which was ramped to 2600°C under maximum-power heating conditions in a 50 W plasma with a self-biased centre electrode.

false-coloured images. The imaging software associated with the CCD permits no direct detailed image analysis (*e.g.*, no spatial integration of emission intensity) and only the highest pixel intensity in the array is readily displayed. As an aid to interpretation of the false-coloured images presented in Figure 49, selected three-dimensional response surfaces of emission intensity are plotted in Figure 50 and a plot of maximum pixel intensity values *versus* time is given in Figure 51. In general, the overall shape of the curve in Figure 51 is similar to that obtained by the PMT-based system used by Sturgeon *et al.* [197].

The initial image in the series is typical of the room temperature He images previously shown for the He I 667.82 nm line (which is devoid of spectral interference) and features the centre electrode and weak outer ring plasmas already noted. Thus, it may be tentatively concluded that this high-temperature series of images should provide a good assessment of the actual He I spatial distribution in the plasma. From 0.8 s to 1.6 s, over which the furnace reaches a steady-state temperature, He I emission intensity generally increases. This arises despite a 3-4 fold lower neutral He number density in the graphite tube and a decreased power coupling to the plasma, as reflected power rises to ~25-30 W in this time period (*i.e.*, the power delivered to the plasma decreases by ~60 %) where it remains for the duration of the transient. Furthermore, the centre electrode plasma increases in thickness, commensurate with the increased mean free path of electrons and increased sheath thickness at the lower He gas density. An additional factor accounting for this enhanced centre electrode plasma intensity is the high negative dc self-bias of the centre electrode. The initial value of the dc self bias is ~-10 V at room temperature and this changes with increasing temperature, reaching a maximum negative value -125 V at

Figure 50. Three-dimensional response surfaces for plasma gas species, including He I, N₂, N₂⁺ and CN gathered using a 390 nm, 10 FWHM interference filter for a blank tube which was ramped to 2600 °C under maximum-power heating conditions in a 50 W plasma with a self-biased centre electrode.

Figure 51. Emission intensity gathered at 390 ± 10 nm *versus* time for a 50 W forward power plasma with a self-biased centre electrode. The intensities are measured from the maximum pixel intensity of the image in the corresponding CCD sequence.

2.0 s. This causes the centre electrode to behave increasingly as the cathode in the system during a given half-cycle thereby enhancing the intensity of the centre electrode plasma (Chapter 3). Comparison of the image at 1.6 s relative to the initial image reveals a decreased thickness of the outer ring plasma, which eventually collapses the 90 μm “dark space”. This may arise as a result of liberation of thermionic electrons from the tube wall. Since dark space thickness decreases as secondary electron production increases [43], its thickness at the tube wall decreases when thermionic emission from this surface becomes significant. At 2.0 s into the transient emission intensity begins to level off and then decreases at 2.8 s. Furthermore, a dramatic decrease in the thickness of the centre electrode plasma occurs at 2.0 s. This is the point in the transient where the dc self-bias of the centre electrode reverses polarity as a consequence of generation of thermionic electrons from its surface, eventually resuming its ~ -10 V “room temperature” value at around 3.2 s. The flux of thermionic electrons from the centre electrode surface is responsible for the decreased centre electrode sheath, analogous to the situation at the tube wall described above. The decrease in the thickness and intensity of the centre electrode plasma may be due to the reversal in polarity of the dc self-bias beyond 2.0 s. Near the end of the transient, from 3.6 to 4.0 s, there is a general “levelling out” of the spatial emission pattern such that it begins to resemble that obtained prior to heating the tube. These factors are likely a consequence of the equalization of temperatures of the centre electrode and the tube wall, resulting in the resumption of a small and constant dc self-bias under these circumstances.

Figures 52 and 53 show the false coloured images and selected three-dimensional response surfaces, respectively, for the He I 388.86 nm line emission intensity in an atomization transient in which the dc bias of the centre electrode was held at +40 V. A plot of maximum pixel intensity *versus* time is presented in Figure 54. This graph does not correlate well with the He line intensities at +38 V centre electrode bias obtained by Sturgeon *et al.* [197]. In the latter study, intensities for a number of He lines first increased to 2 s and then exhibited a precipitous drop, possibly as a result of the formation of a mini-arc which resulted in a loss of the plasma image on the entrance slit of the monochromator [197]. In the present study, He I intensity progressively increased to 3.2 s, after which a decline occurs. The overall He I intensity is lower than that observed for the self-bias case (in agreement with the findings of Chapter 3), consistent with the intensity of the centre electrode plasma decreasing with increasing positive bias. In terms of spatial features, the most striking characteristic is that of expanded radial emission occurring at 0.4 s, in agreement with observations in Chapter 3. “Ring-like” structures form which persist, in general form, throughout the heating transient. The origin of these structures is, at present, unknown and they are detected only when a 0 V or positive bias is imposed on the centre electrode. Their intensity increases with increasing positive bias, while their diameter decreases with increasing positive bias. They may simply be the result of the positive dc self bias of the centre electrode repelling He⁺ from the centre electrode into a region intermediate between the electrode and the wall where they are “held” as a consequence of the reversal of the rf field. The formation of a ring of alternating positive and negative space charge in the annular space has been noted for

Figure 52. False-coloured images for plasma gas species, including He I, N₂, N₂^{*} and CN gathered using a 390 nm peak maximum, 10 nm FWHM interference filter for a blank tube which was ramped to 2600°C under maximum-power heating conditions in a 50 W plasma with a +40 V dc bias imposed on the centre electrode.

Figure 53. Three-dimensional response surfaces for plasma gas species, including He I, N_2 , N_2^+ and CN gathered using a 390 nm, 10 FWHM interference filter for a blank tube which was ramped to 2600 °C under maximum-power heating conditions in a 50 W plasma with a +40 V dc bias imposed on the centre electrode.

Figure 54. Emission intensity gathered at 390 ± 10 nm *versus* time for a 50 W forward power plasma with a +40 V bias imposed on the centre electrode. The intensities are measured from the maximum pixel intensity of the image in the corresponding CCD sequence.

concentric cylindrical corona discharges [238] under an ac field. Additionally, it may be that the positive bias of the centre electrode induces a resonance interaction between the electrons in the plasma and the magnetic field of the rf antenna (centre electrode), which propagates circularly around the circumference of the graphite tube [239], thus creating an environment for the formation of ring-like regions of emission.

Other salient features of the images merit discussion. At a dc bias of +40 V the outer plasma merges towards the wall, producing an intense wall glow, as noted in Chapter 3. Thus, even early in time (at low temperature), unlike Figure 1, no thick outer ring plasma is evident. From 0.8 - 1.6 s the tube wall attains a steady-state temperature and thermionic emission begins from the tube wall. Because the dc bias of the centre electrode is maintained at +40 V, the centre electrode is incapable of repelling the flux of thermoelectrons as effectively as it does in a self-bias run. Thus, electrons emitted from the hot tube wall may more efficiently reach the centre electrode and contribute to an enhancement in intensity in the annular area proximate to it. At 2.0 s the centre electrode has heated up sufficiently to allow thermionic emission from its surface. Because the centre electrode potential is held constant and positive, the centre electrode behaves more as an anode in the system in a given half-cycle. As a result of this, the emitted thermoelectrons are likely more closely confined around the centre electrode area, which explains the decreased centre electrode sheath and plasma region observed beyond 2.0 s. The plasma around the centre electrode actually shrinks, surrounding the electrode tip in some images. The enhancements noted in the annular region from 2.4- 3.2 s likely reflect the influence of thermionic electrons emitted from the tube wall, which may be released

more efficiently into the plasma as a result of the wall acting as a negatively-charged electrode for a greater time in a given rf half cycle. From 3.6 - 4.8 s a decrease in the intensities of all regions of the plasma occurs as the temperature of the tube wall and centre electrode equilibrate.

Several general conclusions can be drawn from Figures 49 to 54. Unlike the HA-FANES source [37], at no time is the plasma extinguished as a consequence of injected thermoelectrons, even for prolonged heating at 2600 °C. This has also been observed previously in monochromator-based measurements of He I line intensities and excitation temperatures during atomization transients [197]. Recently, Le Blanc and Blades [196] have observed the plasma in their FAPES source to extinguish at tube wall temperatures in excess of 1600 K and have suggested that this is the result of thermionic electron emission changing the impedance of the source beyond the range or faster than the response time of their matching network. Since the rf generator and tuner used by these authors is identical to that used in this study, it is evident that the plasma quenching described by Le Blanc and Blades [196] is unique to their system, rather than being emblematic of a general limitation of FAPES. Possibly, the commercial graphite furnace recently employed by these authors [196], with its very high maximum power heating rate of 3500 K s⁻¹ [194], is part of the problem.

Additional information from the false-coloured images reveals that no emission “plume” from the graphite furnace to the sample injection hole is present, despite the increased flux of He towards it during the 0 - 1.6 s when rapid heating of the graphite tube causes expansion of the internal gas out of the injection hole. Also, the absence of a

“plume”-like structure suggests that the contribution of N_2 and CN background species to the image is small, as an emission plume has been observed from one or both of these sources when the tube wall was heated in Chapter 3. Perhaps most importantly, the images presented in Figures 49 and 52 suggest that a relatively small change in the positive dc bias of the centre electrode can produce very significant changes in the He emission “template”, with the formation of an annulus or “rings” of enhanced excitation around the centre electrode plasma. Recent experiments have revealed that a helium FAPES plasma operated at 40.08 MHz has a peak-to-peak rf voltage of only ~ 75 V [240]. It is not unreasonable to assume that an rf voltage of similar magnitude exists in the 13.56 MHz He plasma used in this work. This is particularly significant since the measured rf voltage is more than an order of magnitude less than that previously assumed to exist in FAPES [204]. These small rf voltages suggest that the relatively small dc bias potentials applied to the centre electrode may influence the voltage gradients present in the source and the resulting emission patterns. The implications of changes in the centre electrode dc bias on the atomization of analyte transients will now be discussed.

4.3.2 Effect of dc bias on the Spatial Distribution of Excited-State Atoms during an Atomization Transient

Figures 55 and 56 show the data recorded for atomization of 200 ng of Cu at 2600 °C with a forward rf power of 50 W. The centre electrode was allowed to self-bias (Fig. 55) or was maintained at +25 V (Fig. 56). In the self-bias transient significant Cu I

Figure 55. False-coloured images for 200 ng Cu atomized from the tube wall for a forward rf power 50 W, with the centre electrode allowed to self-bias.

Figure 56. False-coloured images for 200 ng Cu atomized from the tube wall for a forward rf power 50 W, with +25 V dc bias imposed on the centre electrode.

emission begins to appear at 0.45 s and generally fills the tube volume from 0.75 s to 1.25 s before dissipating beyond 1.35 s. The “crescent” at the left side of images from 0.75 - 1.15 s is a (recent) artifact of the CCD chip which becomes most evident when the emission intensity recorded by the chip is high. Positive bias produces enhanced Cu emission directly around the centre electrode, which is particularly evident at 0.85 s and beyond. Bias control (primarily 0 V bias) increases the effective length of the atomization event, possibly by providing a more consistent excitation environment. This was also observed for Fe and Pt by Sturgeon *et al.* [197]. Silver exhibits similar overall excitation effects to that for Cu, with the exception that its distribution more uniformly extends to the walls, consistent with the higher affinity of Cu for graphite surfaces [241].

For comparison with the atomization characteristics of transition elements, the atomization of an easily ionized element, Cs, was examined as bias and power were varied. Figure S7 shows the atomization sequence for 10 ng of CsCl at 2600 °C with a forward rf power of 50 W and a self-biased centre electrode. Emission from Cs I commences from the tube wall at approximately 0.05 s and gradually fills the tube internal volume relatively uniformly, with the exception of the area proximate to the centre electrode. A dark gap remains in this region throughout the duration of the atomization transient. This gap is likely the consequence of Cs ionization within the intense centre electrode plasma. The apparent “intensity” at the centre electrode tip is an artifact of thermal and plasma-induced heating of the centre electrode, which becomes so intense at ~850 nm that complete background correction is problematic. The “rings” of excitation observed for He I in Figure S2 and Cu I in Figure S5 are absent in this self-biased system.

Figure 57. False-coloured images for 10 ng CsCl atomized from the tube wall for a forward rf power 50 W, with the centre electrode allowed to self-bias. The emission observed is primarily from the Cs 1 852.11 nm resonance line.

As the forward rf power to the plasma is increased to 100 W the depletion region around the centre electrode grows, consistent with plasma-induced ionization of Cs in the (expanded) centre electrode plasma. This is illustrated in Figure 58. This plasma-induced ionization process was verified in a subsequent experiment in which 100 μg CsCl was atomized and excited *in the absence of a plasma* at 2600 °C (the higher analyte mass being required to obtain an emission signal in the absence of a plasma). Figure 59 clearly shows that excited-state Cs fills the tube volume reasonably uniformly before dissipating. Furthermore, the entire event is delayed more than 1 s compared to that in the presence of a plasma, indicating the key role the plasma plays in excitation and ionization of Cs. Only at very weak plasma power (20 W) could a condition be realised in which the “depletion zone” due to ionization around the centre electrode was eliminated, owing to the decreased production of Cs^+ in this region. Similar distributions, in terms of ionization depletion and power dependencies, were also observed for Na (whether injected as the chloride or nitrate salt). The “depletion zone” detected for Na was smaller in diameter than that for Cs, as a consequence of the higher ionization potential for Na.

Experiments were also undertaken to determine whether bias control had any effect on the ionization “depletion zone” around the centre electrode. Figure 60 shows the results obtained for 10 ng of CsCl atomized as before into a 50 W rf power plasma with a +25 V bias on the centre electrode. Figure 61 displays the results obtained for a -47 V bias. At +25 V bias the emission rings again form (this is particularly evident when images obtained at 0.15 and 0.20 s in Figure 60 are compared with those at the same time intervals as in Figure 57) and the size of “depletion zone” is enhanced relative to the self-

Figure 58. False-coloured images for 10 ng CsCl atomized from the tube wall for a forward rf power 100 W, with the centre electrode allowed to self-bias. The emission observed is primarily from the Cs I 852.11 nm resonance line.

Figure S9. False-coloured images for 100 µg CsCl atomized from the tube wall at 2600°C without the presence of a plasma. The emission observed is primarily from the Cs I 851.11 nm line.

Figure 60. False-coloured images for 10 ng CsCl atomized from the tube wall for a forward rf power 50 W, with a +25 V dc bias imposed on the centre electrode. The emission observed is primarily from the Cs I 852.11 nm resonance line.

Figure 61. False-coloured images for 10 ng CsCl atomized from the tube wall for a forward rf power 50 W, with a -47 V dc bias imposed on the centre electrode. The emission observed is primarily from the Cs I 852.11 nm resonance line.

bias run shown in Figure 57. For the -47 V bias situation the results are reversed and Cs I emission encroaches much more closely around the centre electrode than for a self-bias run at the same rf input power (although not as closely as the results obtained for 20 W or in the absence of a plasma). Initially, this would appear to be counter-intuitive, since the results presented earlier (Chapter 3) show that the intensity of the centre electrode plasma decreases with positive bias, implying that positive bias should be more favourable for decreasing the extent of Cs ionization. However, positive bias also has the effect of enhancing both the radial emission intensity of the plasma and creating relatively intense annular structures surrounding the centre electrode. Since the "emission event" for Cs ends at ~ 0.4 s, the bias potential at the centre electrode never exceeds ~ -20 V for the images obtained (see the bias curve in Figure 35) in a self-biased run. Thus, a more likely explanation for the dependence of the Cs I emission distribution on the dc bias can be obtained by realizing that a positive bias extends the radial excitation capacity of the plasma such that significant ionization of Cs occurs further away from the centre electrode (*i.e.*, proximate to the "excitation annulus" developed at positive bias) despite a decrease in the centre electrode plasma intensity. A negative bias of -47 V, on the other hand, is more negative than the "indigenous" value obtained in a self-bias run and has the effect of decreasing the intensity of the radial emission region near the centre electrode plasma. Thus, despite an increase in the centre plasma intensity, a decrease in the radial excitation capability of the plasma permits a closer encroachment of Cs I to the centre electrode. This effect may have more practical uses in future applications of FAPES (*e.g.*, as an ion source for mass spectrometry).

Complementary information regarding ionization in FAPES was obtained by directly imaging an excited-state ion population. Calcium was selected for study and emission from the Ca II 393.37 nm and Ca II 396.85 nm lines was isolated using a 10 nm FWHM, 395 nm peak maximum interference filter (see Table 5). Figure 62 displays the results obtained for atomization of 100 ng Ca at 2600 °C into a 50 W plasma with a self-biased centre electrode. Initial arcing of the plasma to the conductive sample deposit is observed at 1.00 s and Ca II emission begins at 1.30 s, progressing radially around the centre electrode from 1.55 s onward. Intense Ca II emission occurs around the centre electrode between 1.6 and 2.0 s. Thus, Ca II emission is concerted primarily around the centre electrode, providing a “mirror image” to the depleted area surrounding the centre electrode observed in the Cs images. This relatively localized Ca II emission pattern reflects the high excitation energy of the Ca II emission lines and is consistent with the data for high-lying transitions (*e.g.*, CO⁺ and N₂⁺ in Figure 45, Chapter 3). Biasing the centre electrode to 0 V or positive voltage results in more enhanced wall emission, in accordance with an expansion of the plasma (0 V bias) and the formation of a wall plasma at positive biases. This characteristic observed for Ca II and Cs I is consistent in ascribing regions of greatest ionization in FAPES as being proximate to the two most intense regions in the system: the centre electrode plasma and the weaker outer ring plasma.

Figure 62. False-coloured images for 100 ng Ca atomized from the tube wall for a forward rf power 50 W, with the centre electrode allowed to self-bias. The observed emission is primarily from the Ca II 393.37 nm and Ca II 396.85 nm lines.

4.3.3 Effect of Easily-Ionized Elements on the Spatial Distribution of Excited-State Analyte Atoms during an Atomization Transient

The effect of 10 μg NaCl on the emission from Cu atomized at 2600 °C into a 50 W plasma with a self-biased electrode is presented in Figure 63. In contrast to the Cu emission transient obtained in the absence of NaCl (Figure 55), there is significant suppression of Cu excitation in the annular region between the centre electrode and the graphite tube wall. This is particularly evident from 0.45 - 0.90 s. Indeed, at these times Cu I emission is generally confined to a region around the centre electrode and the tube wall. This is not that surprising, considering that these regions contain the centre electrode plasma and the outer electrode plasma, which are the most intense regions of excitation. Similarly, the suppression of excitation in the annular space is also not surprising, since the plasma intensity is weakest in this region. Silver, atomized in the presence of EIEs, produces the same pattern of excitation suppression as Cu, although the duration of the effect is longer. This pattern of decreased excitation suggests that it is a consequence of reduced plasma electron energy, or a lowered electron energy distribution function arising from excitation and/or ionization of Na. Beyond 0.90 s greater radial Cu emission is evident, approximating the distribution found in the absence of NaCl. Dissipation begins at 1.30 s. This implies that the most significant vapour cloud overlap between Cu and Na occurs between 0.40 and 0.80 s, which was confirmed by direct CCD imaging of emission from the Na I 589.00 nm and Na I 589.59 nm lines. In any graphite furnace source the degree of vapour cloud overlap between interferent and analyte at a given temperature will

Figure 63. False-coloured images for 200 ng Cu atomized from the tube wall in the presence of 10 μ g NaCl for a forward rf power 50 W, with the centre electrode allowed to self-bias.

determine the extent of the interference effect. As a consequence, one would expect analytes of volatility lower than that of Cu to exhibit a decreased interference effect, whereas more volatile analytes would be more severely affected by the presence of NaCl. For Cu, the above “quenching” of analyte emission patterns begins in the presence of 2.5 μg NaCl and progressively increases until, at 100 μg NaCl, only weak Cu emission around the centre electrode is evident. This is in accordance with the results of Falk [22] who calculated that a concentration of 0.01% NaCl (equivalent to 2 μg in a 20 μL aliquot) would be sufficient to bring about a 10 % power loss in FAPES.

Previous Cu atomization experiments conducted with an HGA-76B power supply revealed that the interference effect manifested itself at much lower NaCl concentrations, with substantial suppression occurring at 5 μg NaCl and essentially complete suppression occurring at 20 μg NaCl (compared with 100 μg NaCl in the HGA-500 system). This is the consequence of the lower maximum power heating rate of the HGA-76B supply relative to the HGA-500 power supply ($\sim 1250\text{ }^{\circ}\text{C s}^{-1}$ vs. $\sim 2000\text{ }^{\circ}\text{C s}^{-1}$) and is consistent with the work of Hettipathirana and Blades [214], who observed significant emission suppressions for Pb at NaCl masses of only 162 ng with heating rate of $90\text{ }^{\circ}\text{C s}^{-1}$. In contrast, Imai and Sturgeon [216], using a nominal $1600\text{ }^{\circ}\text{C s}^{-1}$ heating rate and an identical ICC FAPES source, observed a 50 % *enhancement* in Pb emission signals in the presence of 500 ng of NaCl, which they ascribed to the early volatilization and subsequent plasma-induced dissociation of PbCl. Suppression of the Pb emission signal only manifested itself at NaCl masses of 10 μg or more. These data serve to point out the critical importance of the heating rate of the graphite furnace power supply in affording

a “plug” of atomic vapour to the plasma, readily available for excitation. At low graphite furnace heating rates both plasma and matrix components are slowly “distilled” into the excitation volume.

An additional salient feature of Figure 63, which is common to all the EIE matrices examined in this Chapter (NaNO_3 and CsCl), is the development of an “arc” to the sample injection hole of excited analyte atoms from 0.50 - 0.80 s. This arc forms readily when analytes are atomized in the presence of an EIE matrix or when sufficiently large (*e.g.* 0.2 μg) amounts of EIEs themselves are atomized. It is not significant for atomization of other elements or in non-EIE matrices. For example, atomization of Cu in the presence of only 5 μg NaCl sufficed to produce the arc, but atomization in the presence of 40 μg Fe yielded no arc. Therefore, the formation of the arc must be related to ionization and changes in plasma conductivity. It is interesting that the arc occurs exclusively in the direction of the dosing hole and not to other points along the outer electrode (graphite furnace) surface. The reason for the preferential arc formation to the sample injection hole may be related to the convective flow of He gas inside the graphite tube, or it may simply be an edge effect due to voltage fields near the sample injection hole. When the dosing hole was plugged with a graphite rod, no arc occurred. Note that because the graphite plug protrudes into the graphite tube somewhat, it is conceivable that an “edge effect” may still arise due to perturbations of voltage fields around it as well. Similarly, when Ca is atomized and emission from the ionic state is monitored, no arc forms to the dosing hole. Ionic calcium emission commences at 1.30 s (Figure 62), after the furnace has reached a steady-state temperature and rapid expulsion of He out of the

dosing hole has ceased. The lack of arc formation under these experimental conditions, in addition to when the dosing hole is plugged suggest that arc formation is related to the flow of He and its rapid expulsion from the dosing hole as the furnace reaches a steady-state temperature (at ~ 1 s under maximum power atomization conditions). Imaging of Na transients has shown that, although arc formation accompanies it as well, it has ceased by the time of Cu arc formation and Na is simply present within the volume of the graphite tube (*c.f.* Cs, Figure 57, at 0.15 s). Thus, Cu is not co-vaporized in an arc along with the Na matrix. Arc formation to the sample injection hole observed for Cu is a consequence of the presence of EIE vapour which forms a more conductive path from the centre electrode to the tube wall (outer electrode). Imaging these analyte/interferent systems in an enclosed integrated contact cuvette (ICC) furnace without a flow of gas would prove useful in further elucidating the reason(s) underlying arc formation in EIE matrices in FAPES.

The effect of $7.3 \mu\text{g NaNO}_3$ (equivalent to $5 \mu\text{g NaCl}$) on the emission from 200 ng Cu atomized at 2600°C into a 50 W plasma with a self-biased electrode is shown in Figure 64. Despite the lower mass of EIE, suppression of Cu emission is much more extensive for NaNO_3 than for NaCl . This enhanced suppression from NaNO_3 was a general trend observed for all analytes examined (Ag, Cu, Ca). Indeed, for all images throughout the Cu transient, emission is confined to a small annulus around the centre electrode with only very weak emission being observed near the tube walls and radial emission being almost negligible. The explanation for this may be related to differences in the thermal properties of NaCl and NaNO_3 . Hettipathirana and Blades [214] have

Figure 64. False-coloured images for 200 ng Cu atomized from the tube wall in the presence of 7.3 μg NaNO_3 (equivalent to 5 μg NaCl) for a forward rf power 50 W, with the centre electrode allowed to self-bias.

measured Na emission arising from the vaporization of NaCl and NaNO₃. They concluded that NaCl vaporized early from the tube wall, whereas NaNO₃ vaporized from the tube wall later in time, consistent with a mechanism for formation of Na on the graphite surface by carbon reduction of Na₂O, as proposed by Campbell and Ottaway [242]. When NaNO₃ is used:

When a charring temperature of 1300 °C is employed for the vaporization of Cu in the presence of NaCl, an early arc (at ~0.10 s) arises from the centre electrode to the dosing hole prior to atomization of Cu from the tube wall at ~0.45 s. This is not observed when an equimolar mass of NaNO₃ is used, suggestive of early transfer of molecular NaCl to the centre electrode, which then enables the arc to form more readily. As well, images obtained for equimolar amounts of NaCl and NaNO₃ at high charring temperatures are more intense for the latter salt, suggesting more efficient removal of NaCl at these charring temperatures. On the other hand, NaNO₃ is reduced to Na₂O and then by carbon to metallic sodium on the graphite surface. Hence, the extent of EIE effects for Na (and for other EIEs as well) may depend upon the chemical form in which the EIE is present and its thermochemical properties. If the EIE is present as a less volatile salt (or salt matrix), it will be more efficiently retained within the graphite tube, producing a more pronounced interference effect. Results obtained for NaCl highlight that the beneficial effects of thermal pretreatment (charring) for removal of volatile forms of EIEs will be

more restricted in FAPES than for GFAAS as a consequence of the cooler centre electrode acting as an efficient condensation site for matrix vapour.

Figure 65 shows the effect of the presence of 14.4 μg CsCl (equivalent to 5 μg NaCl) on Ca ion emission for 100 ng of Ca atomized at 2600 °C into a 50 W self-bias plasma. In all images, emission from Ca II is suppressed everywhere except around the centre electrode. The effect of CsCl on Ca II emission is similar to that obtained for NaCl, but more pronounced due to the lower ionization potential of Cs. The suppressive effects of equimolar amounts of CsCl and NaNO₃ are, however, comparable. This last factor suggests that ionization of the Cs does not contribute as significantly to the loss of plasma power as photons radiated from the excitation of Cs and Na. In addition, attenuation of plasma electron energy from excitation and dissociation of molecular matrix species may occur. In general, NaCl, NaNO₃ and CsCl produce the same overall pattern of suppression of excitation for all analytes studied (Cu, Ag and Ca). The extent of the suppression is dependent upon the degree of vapour cloud overlap between analyte and EIE. Cesium should, however, have a greater vapour cloud overlap with analytes at higher temperatures due to the greater involatility of Cs *vis à vis* Na. It should be pointed out that the CCD imaging software does not permit calculation of integrated emission intensities over any region of the image, so no statement concerning the effect of EIEs on spatially integrated signals can be made. However, it is reasonable to assume that the suppressed "emission patterns" observed are reasonable representations of results that would be obtained in monochromator/ photomultiplier (PMT)-based detection systems, from the simple consideration that the analysis volume in such systems consists of a thin

Figure 65. False-coloured images for 100 ng Ca atomized from the tube wall in the presence of 14.4 μg CsCl (equivalent to 5 μg NaCl) for a forward rf power 50 W, with the centre electrode allowed to self-bias. The observed emission is primarily from the Ca II 393.37 nm and Ca II 396.85 nm lines.

slice of the plasma near the centre electrode from the top to the bottom of the graphite tube. Any suppression in radial emission in that slice would thus be manifest as a loss of integrated emission detected by the monochromator-PMT system as well. The fact that suppressions in integrated emission signals have been observed in PMT-based detection systems [214,216] for similar analytes and the same masses and types of EIEs used in this Chapter supports the above assumption.

4.3.4 The Effect of dc Bias on the Spatial Distribution of Excited-State Analyte Atoms in the Presence of Easily-Ionized Elements

DC bias has been shown to significantly influence the spatial distribution of analyte emission in clean matrices and its control affords robustness of excitation temperatures in an atomization transient [197]. Thus, the influence of dc bias in controlling the effects of the “excitation suppression pattern” observed for EIEs in self-bias systems was investigated.

Figure 66 shows the images obtained during atomization of 50 ng Ag at 1700 °C into a 50 W self-bias plasma in a clean matrix, whereas Figure 67 shows those for the atomization of the same mass of Ag with 125 ng NaCl under the same operating conditions. Clearly, extensive suppression of Ag emission throughout the course of the transient occurs at even these low interferent loadings and despite a larger *effective* plasma power (reflected power is 1-3 W at 1700 °C compared to 33-35 W at 2600 °C). The primary reason for this is that, unlike Cu, for which Na vapour overlap occurred for ~0.3

Figure 66. False-coloured images for 50 ng Ag atomized from the tube wall for a forward rf power 50 W, with the centre electrode allowed to self-bias.

Figure 67. False-coloured images for 50 ng Ag atomized from the tube wall in the presence of 0.125 μg NaCl for a forward rf power 50 W, with the centre electrode allowed to self-bias.

s into the 1.0 s transient, CCD imaging of Na I reveals that it persists throughout the entire Ag transient at 1700 °C. Early (0.10 s - 0.20 s) emission of Ag is completely absent, arcing is prevalent and, unlike Ag in a clean matrix, a complete cross-sectional filling of the graphite tube with emission from the Ag I 328.07 nm line is never realized. As with the other analytes and, for reasons already discussed, the magnitude of this effect increases when equimolar amounts of NaNO₃ and CsCl are present.

Figure 68 shows the results obtained for the same interferent and operating conditions as above but with a +25 V bias imposed on the centre electrode. Clear in these images (and also strongly evident for a 0 V bias on the centre electrode) is the development of the “excitation annulus” near the centre electrode, as was observed for He and analytes in clean matrices. Emission in this region is enhanced relative to the self-bias case and the arcing of Ag to the sample injection hole lasting up to 1.0 s under self-bias is essentially absent for the zero or positive bias condition. Applied negative biases produced very pronounced arcs to the dosing hole throughout the atomization transient. The lack of arc formation at 0 V or slightly positive biases (*i.e.*, 12-25 V) compared to self-bias or large negative bias may derive from a more equal polarity between the centre electrode and the outer tube wall during a given half-cycle under these conditions. At 0 V dc bias the centre electrode and tube wall serve as cathode and anode for equal periods of time during a given rf half-cycle, while for a +12 to +25 V bias the tube wall is the anode for only a slightly greater period of time than the centre electrode during a given rf half cycle. Because an arc forms most readily when the difference in polarities of the centre electrode and outer wall are accentuated (*i.e.*, in the self-bias or large negative bias

Figure 68. False-coloured images for 50 ng Ag atomized from the tube wall in the presence of 0.125 μg NaCl for a forward rf power 50 W, with +25 V dc bias imposed on the centre electrode.

case), its formation may be somewhat attenuated under 0 V or small positive bias. Copper and Ca exhibit similar effects. Unfortunately, study of this radial enhancement was restricted to low interferent loadings as application of a positive bias with interferent masses in excess of 0.5 μg NaCl for Ag or 2.5 μg for Cu and Ca produced a sufficiently conductive sample deposit to encourage arcing of the plasma to the sample deposition site.

4.3.5. The Effect of dc bias on the Spatial Distribution of Excited-State Analyte Atoms in the presence of an Iron Matrix

The similarity in suppression effects observed for CsCl and NaNO₃ implies that attenuation of plasma excitation power is primarily a consequence of loss of photons from the excitation of the EIE. To support this, Fe was used as an interferent to see if excitation of its large number of available spectral transitions would bring about a similar suppression in analyte intensity as a result of the photon loss mechanism [22]. The use of Fe is also fortuitous in that its atomic weight is close to the molecular weight of NaCl, thus permitting ready comparison for these two interferents at approximately the same mass loadings.

Figure 69 shows the images obtained during the atomization of 50 ng Ag in the presence of 20 μg Fe at 2600 °C into a 50 W self-bias plasma. Unlike Ag vaporizing from a clean matrix, for which Ag I emission commences at 0.10 s, the onset of Ag I is delayed until 0.35 s in the presence of 20 μg Fe, presumably because Ag is embedded in the less volatile Fe matrix. More significantly, however, the radial distribution of Ag is

Figure 69. False-coloured images for 50 ng Ag atomized from the tube wall in the presence of 20 μg Fe for a forward rf power 50 W, with the centre electrode allowed to self-bias.

altered throughout the entire transient such that the only regions of high Ag intensity are those around the centre electrode and the tube wall. This situation is similar to the radial “excitation suppression” already noted for Ag in the presence of 0.125 μg NaCl, with the exception that there is essentially no arc formation in the presence of Fe, despite the fact that He is being expelled from the dosing hole during the first 1.6 s of both interferent transients. This further illustrates the increased conductivity imparted to the plasma by the sample matrix (*i.e.*, EIE) in being responsible for the formation of the arc to the sample injection hole. A larger mass of Fe than NaCl is required to produce an equivalent matrix effect. For example, whereas only 0.125 μg NaCl produces substantial suppression of radial emission from Ag I, significant suppressions by Fe on Ag I only begin at interferent loadings of 5 μg . Suppression effects for Cu and ionic Ca in the presence of Fe are generally similar to the those observed for Ag, except that a larger (20 μg) mass of Fe is required to produce the onset of quenching of the radial distribution.

Figure 70 contains images which illustrate the atomization of Ag in the presence of the 20 μg Fe into a 50 W plasma with a +22 V bias imposed on the centre electrode. Greater radial emission is evident in all of these images as the development of the radial “excitation annulus” occurs. The general emission pattern is analogous to that obtained for similar bias conditions for Ag and 0.125 μg NaCl, with the exception that formation of excited-state Ag atoms is delayed due to the Fe matrix and the radial excitation pattern is wider in the case of Fe. As with NaCl (or NaNO_3 or CsCl), negative biases were unusable as these produced significant arcing to the sample deposit site. Application of a positive bias up to +38 V decreased the volume of the excitation annulus somewhat (as

Figure 70. False-coloured images for 50 ng Ag atomized from the tube wall in the presence of 20 μg Fe for a forward rf power 50 W, with +22 V dc bias imposed on the centre electrode.

with the EIEs) and, as positive biases in excess of 38 to 40 V tend to cause arcing in clean systems, their influence was not addressed in studies involving interfering matrices. Biasing effects for ionic Ca and Cu were similar to those reported for Ag. The general trend of excitation suppression for all analytes studied in the presence of Fe and the similarity of the spatial response of different analytes in the presence of this interfering element to the dc bias of the centre electrode suggest that the major mechanism underlying the suppressive effects of EIEs on analyte distributions lies in the loss of photons due to the excitation of the matrix (Fe or EIE) and the less energetic plasma which ensues. Although ionization effects likely play some role in analyte suppression, it is probable that this mechanism does not cause a significant energy loss in the plasma, since equimolar amounts of Cs (as CsCl) and Na (as NaNO₃) produce similar quenching effects.

4.4 CONCLUSIONS

The dc bias of the centre electrode plays a significant role in determining the spatial distribution of analyte in the FAPES plasma for both clean solutions and interfering matrices. The reason for this large influence may result from the small voltage (~75 V peak-to-peak) applied to and sustaining the FAPES plasma [240]. As such, the application of an additional, relatively small, dc bias voltage to the centre electrode strongly affects the voltage gradients present in the source and, by extension, the spatial distribution of analyte emission. In the case of Cs, positive bias is seen to have the effect of displacing ionic emission further from the centre electrode whereas negative bias has the opposite

result. Application of a positive bias (or 0 V bias in most cases) is sufficient to cause the formation of ring-like structures near the centre electrode plasma. This additional annulus of emission occurs for He and for analytes in the presence and absence of EIEs.

Easily ionized elements quench the annular analyte emission. This occurs most extensively when the centre electrode is allowed to self-bias. In the presence of EIEs, (analyte) expulsion is visibly detected early in time as an arc to the dosing hole since He is being rapidly expelled from the volume of the graphite tube prior to the attainment of a steady-state temperature. A similar arc does not form in the presence of an iron matrix, indicating that plasma conductivity is altered in the presence of EIEs. With the centre electrode allowed to self bias, interference effects in terms of radial suppression by Fe parallel those observed with EIEs, although a greater mass of Fe is required to induce comparable interference effects. Control of the dc self-bias of the centre electrode decreases the extent of radial emission suppression by both EIEs and Fe, with 0 V or slightly positive biases (+12 to +25 V) generally affording the greatest degree of recovery of annular emission. The utility of bias control is limited to low interferent loadings ($\leq 2 \mu\text{g}$, generally), otherwise arcs and instabilities begin to manifest themselves. It should be stressed, however, that limitations which the current CCD imaging system do not permit integrated emission intensities to be obtained. Further investigation will be required (*e.g.*, with conventional PMT detection) to ascertain the full extent of some of the suppressions and enhancements observed.

CONCLUSIONS AND SUGGESTIONS FOR FUTURE RESEARCH

The objectives of this research were to study glow discharge plasmas at reduced and atmospheric pressure as sources for analytical atomic spectrometry. Some general trends are apparent with respect to the low pressure glow discharge atomizer. The response surface of this atomizer is quite complicated due to the presence of the gas jets and the long path length created by the pumping ports. Although the jets are effective in reducing the degree of redeposition and thereby enhancing effective sputtering yields, the amount of added sputtered neutrals to the glow discharge plasma makes self-absorption and, ultimately, self-reversal, problematic for commonly-used resonance analyte transitions. While it was assumed that self-absorption/reversal effects may be confined exclusively to such jet-assisted atomizers, Winchester and Marcus [156] recently observed strong self-absorption/reversal effects for the Cu I 324.75 nm line in a non-jet assisted glow discharge atomizer of completely different design to that used in these studies. This suggests that self-absorption of resonance atomic lines may be a problem for glow discharge atomizers in general and that further investigations to determine how atomizer design (*i.e.*, orifice diameter, cell volume, location and number of pumping ports) contributes to these effects are urgently required. Alternative analysis lines (*i.e.*, non-resonance transitions) other than those which are currently (and commonly) used in emission spectrometry could be selected to minimize self-absorption effects. Since the response of these non-resonance transitions to operating parameters has generally not been extensively studied in glow discharge spectrometry, line selection and parametric

evaluation of how the use of alternative lines impacts analytical figures of merit is also required so that rational and methodical line selection protocols may be developed, analogous to those already in existence for ICP-AES [243]. The results of Chapter 1 of this thesis also suggest that a single glow discharge design for multitechnique application (*i.e.*, absorption, emission, fluorescence, mass spectrometry) is likely not feasible due to the conflicting requirements of these methods of measurement and that the design of the atomizer must be carefully “tailored” to the requirements of the technique.

With respect to atmospheric pressure glow discharges used for analyte excitation, the FAPES source was shown to have significant spatial concentration gradients both for plasma gas species and atomized analytes. The existence of an outer ring plasma proximate to the wall and its response to alterations in the applied dc bias voltage of the centre electrode suggests that, to a first approximation, FAPES can be viewed as a rapidly oscillating dc glow discharge at atmospheric pressure. Furthermore, the dc bias response to the system with analytes in empty tubes and in the presence of matrix species is quite marked, enabling regions of preferential excitation to be created by the application of the appropriate bias potential. The fact that applications of tens of volts (positive or negative) dc bias can produce a marked change in plasma characteristics suggests that the voltage in the FAPES source is much smaller than the 1000 V commonly assumed [204]. Recent experimental measurement of peak-to-peak rf potentials of the order of 75 V [240] suggests that bias control, or at least bias measurement, is an important consideration in improving the reliability and applicability of FAPES for common analytical use. Although bias manipulation may only be of limited use in ameliorating deleterious matrix effects,

the fact that the degree of Cs ionization can be somewhat controlled spatially by the application of bias suggests that this parameter may be of use in eventual development of FAPES as an ionization source for mass spectrometry, the utility of which was first proposed by Banks *et al.* [206].

Future FAPES investigations should focus on the discharge formed in an integrated contact cuvette (ICC) furnace enclosed within a vacuum 6-way cross chamber. Such a system is useful for exclusion of atmospheric components which can attenuate plasma electron energy. The more isothermal environment and lack of a directed internal purge gas flow would serve as a useful comparison to the work reported in this thesis for Massmann-type graphite furnaces. Argon FAPES plasmas have higher electron densities than their He counterparts [244] and this may prove attractive to “buffering” the effects from EIEs. Thorough two-dimensional characterization of Ar plasmas at generator frequencies of 27.12 MHz and above is warranted. Investigations of higher plasma frequencies in both He and Ar is of interest since such systems would be expected to dissipate more power into the plasma [218], augmenting analyte excitation. The dc bias in low pressure glow discharges has been shown to depend on operating frequency [201] and the response of this parameter in FAPES to both operating frequency and discharge gas is of interest.

Finally, this thesis has shown that the CCD imaging system in its current state of development [222] lacks both sensitivity and spectral selectivity in comparison to conventional monochromator/PMT detection. While this does not invalidate the utility of the data derived from it, it necessitates use of sample masses one to two orders of

magnitude greater than those used in analytical practice. Additionally, the wide spectral bandpass of the system (10 nm) can exclude study of particular analysis lines or line combinations as the result of spectral overlap. Investigations of highly complex matrices may be completely precluded because of this. For example, although the CCD system offers adequate background-subtraction capability to enable the investigation of single salt matrices, the use of Pd as a modifier in reducing matrix effects may be precluded because of the preponderance of strong Pd lines throughout the spectrum which overwhelm analyte emission intensity.

These problems may, in principle, be overcome through the use of intensified CCD (ICCD) detectors which are electronically gated and can provide enhancements in low light amplification up to two orders of magnitude over non-intensified CCDs [245]. If an ICCD-based imaging system were implemented, CCD imaging currently done with 5 ng - 1 μ g masses of analyte could approach the 50 pg to 5 ng amounts used with PMT detection. The limited spectral resolution of the current apparatus could be addressed with the introduction of a (non-collinear) acousto-optic tunable filter for ultraviolet (UV) wavelength selection, having bandpasses in the range 0.1 - 0.6 nm [246]. An AOTF-ICCD system for time-resolved imaging of laser-induced plasma plumes in the visible-UV region was reported by Multari *et al.* [247]. This AOTF system, however, incorporates a TeO₂ crystal, the optical throughput of which is unsuitable for far-UV applications [246]. AOTFs based on quartz (collinear) and MgF₂ piezoelectric substrates exist, but the photoacoustic figures of merit of these materials are poor, with the result that the optical throughput of these devices approaches those of far-UV interference filters (~10-15 %).

If the increased sensitivity theoretically attainable with ICCDs becomes achievable in practice (such systems are limited by high read noise), the low throughput of the AOTFs may be counterbalanced sufficiently to permit reliable measurements of low analyte masses with high spectral selectivity.

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