EVOLUTION AND EVALUATION OF A JET-ASSISTED GLOW DISCHARGE SOURCE FOR ATOMIC EMISSION SPECTROMETRY

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Abstract

Glow discharge atomic emission spectroscopy is a useful analytical method for the direct analysis of conducting solids thereby obviating the need for time-consuming and hazardous dissolution procedures common with other methods. Detection limits for analytical glow discharges, however, are restricted to relatively high analyte concentrations when compared to other methods. One aspect of glow discharge sampling which proves adverse to analytical performance is through significant analyte loss before excitation by the re-deposition of sputtered species back onto the sample surface.

Sputtered atoms are typically ejected from the sample surface with a range of energies that extends to 20 eV, however, this ejection energy is quickly thermalized by collisions with support gas species at pressures typically used for analyses. As a consequence, sputtered atoms are readily re-deposited back onto the sample surface, primarily due to diffusion. For a glow discharge using a planar diode electrode geometry, operating at pressures typically used for analytical purposes, up to 95% of sputtered species re-deposit on the sample surface. Therefore, any method that retards re-deposition would significantly increase the atomization efficiency of glow discharges and increase the sensitivity of the technique.

This work addresses the re-deposition problem using a jet-assisted source that relies on a directed support gas flow that not only aids sample transport to the excitation region, but impedes re-deposition. The original design has gone through a three-stage evolution: each stage correcting certain imbalances found for the
previous model which culminates in an emission source capable of sub-ppm level limits of detection and a precision of less than 0.3 % for certain elements.

A comprehensive study for the jet flow effects on the sample surface, using Scanning Electron Microscopy and Energy Dispersive X-ray Fluorescence, and the emitting plasma, using atomic emission and absorption spectroscopies, has been conducted. In addition, excitation processes have been studied in the jet-assisted plasma plume as it issues from the anode housing. Results indicate that the dominant atomic excitation process is through electron excitation. The electrons originate from the collision of two argon atoms which reside in metastable states.
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CHAPTER 1

INTRODUCTION

1.1 Gas Discharges

In order to understand the glow discharge, it may be expedient to first consider gas discharges on the whole. A gas discharge is said to occur when charged gas phase particles are driven by an electric field. The electrical characteristics of the discharge are a means of classification (Fig. 1.1).

When the discharge carries less current than a picoamp, it is classified as a TOWNSEND discharge and must rely on extraneous ionization sources, such as cosmic radiation, since the electric field is too weak to initiate the ionizing collisions necessary for discharge maintenance. After Breakdown, the electric field provides enough energy for electrons to ionize support gas particles upon collision. The large production of charge carriers at this point drops the resistance between the electrodes significantly causing an overall decrease in discharge voltage with an increase in current of about seven orders of magnitude until a self-sustaining discharge is achieved, called a glow discharge.

The glow discharge with normal cathode fall is characterized by a constant potential with increasing current flow due to incomplete coverage of the cathode by the discharge. Once the glow covers the entire cathode, the current density must increase with current flow and is characterized by an increase in discharge voltage identifying the glow discharge with abnormal cathode fall. As current flow
Figure 1.1: Schematic representation of the electrical characteristics of a gas discharge. Voltage is on a linear scale, current on a logarithmic scale. Adapted from [63].
increases in the glow discharge with an abnormal cathode fall, the discharge voltage increases providing positive ions with more energy at impact with the cathode. The energetic ion is either back-scattered from a surface atom or penetrates into the selvage (first few atomic layers) of the solid where its potential energy can liberate secondary electrons and its kinetic energy can cause surface atoms to be ejected provided the amount of energy transferred exceeds the binding energy of the surface atoms. This phenomenon is called sputtering. Any further increase in current carried by the discharge will eventually lead to localized thermal evaporation of cathode material and the onset of the arc discharge identified by low voltages dropped between electrodes, and high current flows, albeit through a localized channel.

The TOWNSEND discharge has little analytical utility as a sampling device although it is used extensively in pressure metering devices for high vacuum apparati [86]. The arc discharge has been used extensively for analytical purposes due to the possibility of atmospheric pressure operation and copious sample atomization although it is prone to arc wander producing imaging difficulties when used as an emission source [81]. The Spectrojet III, however, is a three electrode dc arc system that analyses liquid samples with acceptable analytical performance [123]. The glow discharge, however, is arguably a superior analytical emission source for direct solids analysis due to the high precision and controllability of the sputtering process and the high emission line to background ratios provided by excitation in the negative glow.
This analysis of gas discharges driven by a direct current electric field has indicated that the glow discharge is perhaps the best suited to solids analysis, however, an understanding of this discharge is still cursory in this manuscript. In the following sections, a brief history of the source and a more thorough description of the physical processes that govern the glow discharge will be presented.

1.2 Historical Development of the Glow Discharge

Low pressure glow discharges are noted for their long history. The advent of scientific interest in these discharges closely paralleled advances in vacuum technology. GEISSLER's mercury pump and his innovative techniques for the construction of glass discharge tubes containing metal electrodes in the late 1850's paved the way for future glow discharge experimentation by such notable scientists as HITTORF and CROOKES in the latter part of that century.

In 1916, PASCHEN replaced the typical planar cathode of a GEISSLER discharge tube with an aluminum foil bent such that it formed a hollow, box-shaped cylinder [88]. He found that the glow from the helium support gas at suitable conditions was entirely contained within the cylinder. The increased luminosity of this lamp allowed thorough study of the helium ion spectrum and PASCHEN found that his empirical results correlated well with BOHR'S theoretical postulates on the structure of the atom. PASCHEN'S work marked the birth of the hollow cathode discharge, an emission source that enjoys widespread use as a line source for atomic absorption techniques since the 1960's.
When used for the direct analysis of metals, however, hollow cathode discharges suffer from the need for some degree of machining of the sample to form the hollow cathode. This, in part, led to the development of the GRIMM glow discharge, or hollow anode discharge, in 1968 [56]. This source has achieved greater popularity compared to the hollow cathode discharge due to its use of a planar cathode (sample) thus reducing the need for any machining of the sample prior to analysis.

There have been many efforts to improve both the sputtering and excitation ability in the hollow cathode and GRIMM glow discharges in the recent past. Both sources have had magnets incorporated into their designs [29, 73] in an attempt to increase both these parameters. The applied magnetic field forces the free electrons in the discharge to undergo a more complex motion that increases their displacement through the negative glow making an exciting or ionizing collision more probable. Although the magnet does indeed increase both parameters, it renders the source sensitive to the magnetic properties of the sample and can produce different calibration curves depending upon whether the samples are magnetic or nonmagnetic [73]. Auxiliary excitation of the negative glow by secondary d.c., radio-frequency, and microwave discharges has also been attempted in both the hollow cathode [29] and GRIMM glow discharges [46]. Although enhanced excitation of sputtered atoms is evident, the auxiliary discharge interferes with the sputtering ability of the primary discharge leaving room for future experimentation and design improvement.
The glow discharge is still attracting much scientific interest as an emission source today as evidenced by many recent publications in the literature [9, 10, 40, 42, 91, 97, 109-111]. This popularity stems from some unique advantages inherent with the glow discharge which will be discussed in the following sections.

1.3 The Glow Discharge

Figure 1.2 portrays a GEISSLER tube containing a low pressure gas, typically at several hundred Pa, which sustains a glow discharge due to the application of a potential difference of approximately several hundred volts between the two electrodes. Upon inspection, various luminous and dark regions are apparent due to the physical processes occurring in the discharge. These physical processes may be better understood by examining the voltage, electric field and net space charge (localized spatial areas of net positive, or negative, charge accumulation) variation with axial position curves aligned with the GEISSLER tube schematic.

The net space charge curve indicates a large positive space charge located near the cathode surface. This phenomenon is due to the different mobilities of the charged particles in the discharge. Positively charged particles (support gas ions), which are relatively heavy, move slowly in the applied electric field when compared to negatively charged particles (electrons), which are relatively light. The formation of this space charge perturbs the electric field causing almost all the potential to be dropped a short distance from the cathode surface. This distance essentially marks the boundary
Figure 1.2: Schematic representation of a glow discharge contained in a GEISSLER tube and voltage, electric field and net space charge variation with axial distance. Adapted from [63].
between the cathode dark space and negative glow and produces a strong electric field which can accelerate support gas ions towards the cathode.

As the support gas ions strike the cathode, the impact can either sputter cathode atoms if they possess sufficient energy, or liberate electrons from the solid, a process called secondary electron emission. Secondary electrons can also originate from the impact of light photons and fast neutrals, although positive ions are the primary source of these particles in glow discharges. Upon emission from the cathode, electrons are accelerated through the ASTON dark space by the strong electric field. Before they absorb much energy, a portion re-combine with incoming positive ions to produce the luminous region called the cathode glow. The electric field is sufficiently strong, however, to accelerate the electrons only a short distance before their velocities are such that the re-combination cross-section for with incoming positive ions is very small. This explains the relative brevity of the cathode glow.

These fast electrons experience few collisions until the electric field weakens and the accelerating force driving the electrons towards the anode is essentially removed. This removal is due to the fact that the positive space charge, caused by a concentration of positive ions, is being replaced by a negative space charge due to the high density of electrons. This marks the end of the cathode dark space and beginning of the negative glow.

In the negative glow, electrons are no longer accelerated and their kinetic energy is consumed by intense excitation and ionization of discharge species causing the brightness of this region. As the
electrons are slowed, the negative space charge reaches a maximum and no further energy is available for excitation or ionization. Therefore the luminous negative glow dims and the FARADAY dark space begins. In this region, the electron density is reduced by recombination and diffusion until the net space charge is zero and the electric field is characterized by a small constant value, typically a few V cm$^{-1}$ [77] marking the beginning of the positive column.

The positive column represents the only true plasma in the glow discharge since only in this region does the net space charge equal zero. Although cross-sections for excitation and ionization are appreciable in this region, it is far enough removed from the cathode surface to significantly reduce the number of sputtered species reaching the positive column. Therefore, the positive column is typically used for plasma physics studies [45] rather than as an analytical emission source. Near the anode, a small negative space charge develops due to the attraction of electrons from the positive column. The acceleration of these electrons forms a thin dark space in front of the anode glow which is caused by the collection of the electrons by the anode. For a more complete description of the processes occurring in the various regions of the glow discharge, the reader is referred to references [77] and [63].

For analytical purposes, the only relevant regions in the glow discharge exist between the cathode surface and the negative glow. If the anode is brought into the negative glow, no appreciable change is seen in the electrical characteristics of the discharge due to the fact that almost all the voltage is dropped between these two regions. Most commercial glow discharge emission sources have their anodes
positioned such that the positive column is eliminated and the only visible luminous region is the negative glow. The aspects of the glow discharge which find practical application are discussed in the next section.

1.4 The Glow Discharge as a Practical Source

The sputtering of cathodes has many applications: it was first used for the deposition of thin films in the electronics industry as early as 1928 for the manufacture of phonograph records [51]. Since then, sputtering has been extensively used in the semiconductor industry in not only thin film deposition, but also surface cleaning and etching of electrical components [104]. However, analytical chemists are more interested in sputtering as a solids sampling tool due to the easily controllable removal of atoms from the cathode surface.

The glow discharge is an additionally attractive device to analytical chemists due to the existence of a region in close proximity to the cathode surface where electrons emitted from the cathode possess sufficient energy to excite and ionize sputtered atoms. This region is called the negative glow and enables the glow discharge to be used as a spectroscopic source.

1.5 The Glow Discharge as an Analytical Tool

Cathodic sputtering is perhaps the most attractive glow discharge feature to analytical chemists since it can provide direct atomization of solid samples without the need for time-consuming and hazardous dissolution procedures prevalent with other analytical methods. Most d.c. sputtering applications require a conducting
sample, although the analysis of non-conducting powders can be accomplished by mixing the sample with a suitably conducting host matrix, like copper powder [21].

Since the material volatilized is essentially ground state atoms, glow discharges are suitable atomizers for detection by atomic absorption and fluorescence. GATEHOUSE and WALSH were the first to use sputter atomization for atomic absorption spectrometry [53]. Contributions from a colleague some years later demonstrated that the use of an internal standard improved the precision of glow discharge analyses involving samples in real matrices [78]. A particularly interesting glow discharge apparatus was the non-dispersive resonance fluorescence spectrometer developed by HUMAN et al. [64]. This spectrometer incorporated a GRIMM glow discharge as primary source containing the sample to be analyzed as its cathode. A second glow discharge is used as a source which contains a pure hollow cathode composed of the sought after element. Since the fluorescence detected is directly proportional to the intensity of the incident radiation from the primary source, quantitative analyses of the GRIMM cathode are possible.

These techniques inherently incorporate a high degree of selectivity due to the use of a primary source which minimizes the spectrometer requirements consequently providing an analytical method which is relatively cheap. However, trade-offs exist: these techniques can only perform sequential analyses which drastically reduces productivity.

The negative glow is also analytically important since it is an efficient excitation medium allowing the region to be used as an
emission source. Atomic emission techniques are noted for their simultaneous multi-element capability and large dynamic range which can drastically improve sample throughput and therefore, productivity. The negative glow is particularly advantageous in that the non-thermal nature of the discharge provides high emission line to background intensity ratios.

The GRIMM glow discharge is arguably the most popular glow discharge emission source (Fig. 1.3). The GRIMM design incorporates a hollow, cylindrical anode that is brought to within a mean free path of the cathode (sample). This allows the formation of the discharge only within the boundaries of the hollow cylinder formed by the anode. In this sense it is an obstructed discharge: the transition from normal to abnormal glow discharge is very efficient since the inner circumference of the anode, which determines the sample area exposed to the discharge, is typically less than 1 cm$^2$. The positioning of the anode also prevents the formation of the positive column: only the cathode dark space, negative glow and FARADAY dark space are present. Unlike the hollow cathode glow discharge, electrons can not undergo multiple passages through the discharge, therefore the GRIMM design is not noted for an increased luminosity. Rather, its popularity stems from the ability for rapid sample replacement. The sample provides the vacuum seal so that the only requirement is that it be flat.

FALK et al. have used a hollow cathode glow discharge in a novel manner. Their source does not rely on sputtering to provide atomization, but rather on the electrothermal evaporation of sample residue. They used a graphite furnace, acting as both furnace and
Figure 1.3: Schematic diagram of the GRIMM glow discharge source. Adapted from [18].
hollow cathode, to provide comparable if not superior detection limits relative to more conventional methods with the FANES (Furnace Atomic Non-thermal Excitation Spectrometry) device [41].

Other atomic emission techniques that utilize both sputtering and negative glow excitation abound in the literature as already indicated. BERNERON has demonstrated that this combination is particularly useful in surface analysis [13]. Since the sputtering process is characterized by the easily controllable layer by layer removal of surface atoms, high resolution depth profiling of the sample is possible. As a result, glow discharge optical emission spectrometry has found applications for the quality control in the composition and thickness of surface coatings on steel [72] and aluminum [93].

The negative glow also contains sufficiently energetic electrons and support gas atoms in metastable states which are capable of ionizing sputtered atoms. The population of ionized sputtered atoms is sufficient for the glow discharge to be used as an ion source for mass spectrometry. Mass spectrometric detection, like atomic emission methods, lends itself to near-simultaneous multi-element analysis, but is also characterized by lower detection limits, simpler spectra and the availability of isotopic information. HARRISON and co-workers were the first to interface a glow discharge to a quadrupole mass filter [11]. Although the analytical performance was promising, they found a preponderance of interfering atomic and molecular ions which could not be separated by the low resolution mass analyzer. Later studies improved upon this performance, but did not eliminate the problems [57]. For this reason, the first commercial glow
15
discharge mass spectrometer, offered by VG ISOTOPES, incorporated
a high resolution double sector instrument. However, this resolution
is achieved at a significantly greater cost making it inaccessible to
most research laboratories.

1.6 Atomization, Excitation and Ionization in the Glow Discharge

Figure 1.4 demonstrates the processes of atomization, excitation and ionization that occur in a low pressure glow discharge. Atomization of cathode atoms is performed by sputtering. Sputtering results from impacting positive ions driven by the electric field present in a glow discharge with abnormal cathode fall. With an abnormal cathode fall, the cathode is completely covered by the discharge and increases in current density produce an increase in the cathode fall potential. This provides a greater electric field and supplies impacting ions with sufficient energy to exceed the sputtering threshold of most cathode materials. For impacting ions with energies below 1 keV, typical for analytical applications, sputtering is thought to occur by elastic collisions occurring in the selvage of the cathode [95]. The bombarding ion transfers its energy to cathode atoms which, after having undergone a small number of additional collisions in the selvage, can be back-scattered to eject surface atoms provided the surface binding energy is exceeded.

Sputtering yields are not uniform for all the elements: in a multi-element cathode, some are sputtered preferentially, but the range in yield for transition metals, with the exception of silver, is less than a factor of five for mono-energetic impacting ions; with inclusion of silver, the range is extended to an order of magnitude [31]. This
Figure 1.4: Schematic representation of sputtering, atomic excitation and ionization in the glow discharge with abnormal cathode fall.
relatively non-selective atomization contrasts significantly with evaporation rates for many elements at specific temperatures. For example, aluminum and tungsten possess evaporation rates that differ by nine orders of magnitude at 2000 °C [113].

The majority of sputtered species exist as ground state atoms and are ejected from the cathode surface with energy distributions which have been shown to tail off to insignificant levels beyond 20 eV [103]. Even sputtered atoms from the high energy tail of the distribution are thermalized a short distance from the cathode by collisions with support gas atoms so that the transport of sputtered atoms to the negative glow is diffusion controlled [101].

Excitation and ionization of sputtered species primarily occurs in the negative glow. This region is relatively field-free and is located adjacent to the cathode dark space where accelerated electrons become thermalized by collisions with support gas atoms, or more importantly for the analysis of cathode material, with sputtered atoms. The electron energy distribution in the negative glow is known not to possess a MAXWELL distribution due to the occurrence of more than one group of electrons. Near the border between the cathode dark space and negative glow, some electrons have accumulated a significant proportion of the energy available from the electric field such that their energy spread may reach 200 eV. Even though the collision cross-sections between these electrons and negative glow species is small, the density of these species is sufficient to slow the fast electrons by inelastic collisions a short distance into the glow so that their energy spread is limited to several decades of electron volts [30]. It is this second group of electrons, which have been slowed but
not thermalized, which is responsible for the majority of excitation and ionization in the glow region. A third group of electrons exists, so-called ultimate or thermalized electrons, which are primarily responsible for re-combination processes.

The negative glow is known not to be in local thermal equilibrium (LTE) largely due to the existence of the non-MAXWELLIAN electron energy distribution [22]. Electron temperatures obtained from probe measurements are characteristically up to an order of magnitude greater than spectroscopically determined excitation temperatures which are in turn almost an order of magnitude greater than kinetic gas temperatures elucidated from DOPPLER broadening (see Table 1). For this reason, glow discharge spectra are dominated by the most sensitive emission lines and characterized by high line to background emission intensity ratios.

1.7 Re-deposition

Although the low pressure glow discharge is a versatile solids sampling tool allowing detection by absorption, fluorescence, emission and mass spectrometry, some problems are associated with the technique. The low pressure operation makes sample replacement a particular chore and the cracking of pump oil vapor by support gas ions can inhibit sputtering of some samples [18]. Perhaps the major problem, however, is the re-deposition of sputtered species on the cathode surface.

It has been reported that up to 90% of sputtered atoms redeposit onto the surface of the cathode for a 0.1 torr discharge sustained between parallel plate electrodes [61]. This pressure is an
Table I: Various temperatures reported for low pressure d.c. hollow cathode and GRIMM glow discharges

<table>
<thead>
<tr>
<th>Source Type</th>
<th>Plasma Conditions</th>
<th>Temperature Measurement</th>
<th>Value (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hollow Cathode [84]</td>
<td>Ar 1 torr, = 10 W</td>
<td>Electron</td>
<td>Cu: 26000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ni: 23000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Steel: 9600</td>
</tr>
<tr>
<td>Hollow Cathode [85]</td>
<td>Ar 2 torr, = 10 W</td>
<td>Excitation</td>
<td>Fe I: 3100-3200</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ar I: 2000-2900</td>
</tr>
<tr>
<td>Hollow Cathode [38]</td>
<td>He 2-16 torr, 0.1-0.3 A Rotation (OH)(^a)</td>
<td>R(_2)(1)-R(_2)(7): 1070-1760</td>
<td>R(_2)(7)-R(_2)(14): 4100-4700</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>R(_2)(14)-R(_2)(20): 6200-8000</td>
</tr>
<tr>
<td>Grimm [26]</td>
<td>Ar 11 torr, 75 W</td>
<td>Ion</td>
<td>Ar II: 30000</td>
</tr>
<tr>
<td>Ibid</td>
<td>3% N(_2) in Ar at 8 torr, 50 W</td>
<td>Vibration</td>
<td>N(_2)(^+): 2900</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>N(_2): 8600</td>
</tr>
<tr>
<td>Ibid</td>
<td>Ibid</td>
<td>Rotation</td>
<td>N(_2)(^+): 2480</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>N(_2): 975</td>
</tr>
<tr>
<td>Grimm [27]</td>
<td>Ar 8 torr, 75 W</td>
<td>Ion</td>
<td>Fe II: 19600</td>
</tr>
<tr>
<td>Ibid</td>
<td>Ar 11 torr, 75 W</td>
<td>Fe I Excitation</td>
<td>Group (^b): 3680</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Group (^c): 3740</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Group (^d): 5540</td>
</tr>
<tr>
<td>Grimm [115]</td>
<td>Ar to maintain 1 kV, current: 50 mA</td>
<td>Doppler</td>
<td>Cr: 1400</td>
</tr>
<tr>
<td>Side-view Grimm [47]</td>
<td>Voltage: 800 V, current: 60 mA</td>
<td>Doppler</td>
<td>Cr: 1500</td>
</tr>
</tbody>
</table>

\(a\): Rotational temperature using the OH (0,0) band of \(^2\Sigma^+ \rightarrow \(^2\Pi^+\) transition and rotational lines of the R\(_2\)(K) branch; \(b\): resonance lines; \(c\): lower energy levels of 0.86 eV; \(d\): lower energy levels of 2.40 eV; \(e\): lower energy levels of 2.18 eV.
order of magnitude less than those typically used in analytical glow discharges. Re-deposition studies have not been performed on analytical parallel plate glow discharges at pressures above 1 torr, although BRUHN and HARRISON have calculated that approximately 94% of sputtered atoms are re-deposited on the target cathode [24]. FERRIERA and BÜGER have reported re-deposition studies for a GRIMM glow discharge and estimated that 17% of copper atoms sputtered are re-deposited [48]. This low value for re-deposition relative to the parallel plate discharge may be due to the additional vacuum port on the GRIMM source which pumps on the cathode region. Although the amount of sputtered atoms re-depositing on the cathode is reduced, a large percentage is still lost to the system before excitation in the negative glow is possible. Therefore, one would expect that any mechanism that not only retards the re-deposition process, but also aids in the transport of sputtered species to the negative glow would significantly increase the atomization efficiency of the glow discharge.

1.8 GOUGH'S Sputtering Cell

In 1976, GOUGH reported a new type of glow discharge that inadvertently addressed the re-deposition problem [54]. The sputtering cell was initially designed to facilitate the sputtering of aluminum, made difficult by the tenacious oxide layer which forms on the surface with exposure to oxygen. However, during the investigation of the characteristics of the source, it was found that the cell produced a higher density of atomic vapor relative to more conventional sputtering cells.
Figure 1.5: Schematic diagram of the GOUGH cell and an enlargement of the hollow silica annulus which admits support gas into the cell parallel to the sample surface. Adapted from [54].
The cell uses a hollow silica annulus to confine the discharge to a small area on the surface of the cathode (Fig. 1.5). Support gas is introduced into the cell through a small gap 0.1 mm in width located in the hollow annulus 0.5 mm from the sample surface. The introduction of support gas is in a direction parallel to the cathode surface, but due to the confinement provided by the hollow annulus, the resultant flow direction is away from the cathode surface. The small gap width introduces support gas into the cell at high speeds: GOUGH estimated a speed of 30,000 cm/sec for a 0.3 L/min flow rate at 5 torr, which being on the same order as the average thermal speed of sputtered metal atoms in the discharge, not only retards the diffusion of sputtered atoms back onto the cathode but aids in their transport to the center of the sputtering chamber. This is evident from the spatial distribution of atoms in the sputtering chamber for both a fast gas flow and a static system.

1.9 The ATOMSOURCE™

Recently, a new version of sputtering cell which makes use of the principle of directed support gas flows introduced by GOUGH has become commercially available [14]. The cell is manufactured by ANALYTE CORPORATION (Grants Pass, OR) and is called the ATOMSOURCE™. The ATOMSOURCE™ uses a geometry which is similar to the GRIMM design in that a hollow anode is brought to within a support gas mean free path of the cathode providing an obstructed glow discharge. However, it differs from the GRIMM design in that support gas is directed onto the surface of the cathode through a
Figure 1.6: Schematic diagram of the six jet ATOMSOURCE\textsuperscript{TM}, adapted from [14].
hexagonal arrangement of jets located between the hollow anode and an insulator (Fig. 1.6).

The ATOMSOURCE™ differs from the GOUGH design regarding the initial direction of the directed support gas, although in both designs the resultant flow after mixing is away from the cathode. In addition, rather than introducing the gas through a gap that runs the full circumference of the hollow annulus as in GOUGH'S design, the ATOMSOURCE™ uses a hexagonal arrangement of six jets. The jets are situated approximately 1 mm above the cathode surface which is twice the distance relative to the support gas introduction gap in the GOUGH cell; however, since the flow is directed at the sample, it is probable that the resultant flow away from the cathode is established at approximately the same area.

The support gas flow impinging on the sample produces a hexagonal arrangement of craters, reflecting the jet geometry, which are significantly deeper than the rest of the burn spot as attested by cross-sectional depth profiles [87]. This suggests that sputtering rates are enhanced where the jets impinge upon the sample.

1.10 GOUGH'S Cell versus the ATOMSOURCE™

A comparison of analytical characteristics between the ATOMSOURCE™ and GOUGH'S sputtering cell was the subject of a report recently published by GOUGH et al. [55]. It was found that the ATOMSOURCE™ yielded absorbances more than a factor of three greater than GOUGH'S cell. However, the lower absorbance was attributed to the geometry of GOUGH'S glass vessel: the ATOMSOURCE™ provides a greater absorption path length due to
more efficient sweeping of atoms along the optical path. This argument is verified by results obtained by housing GOUGH'S hollow silica annulus in a T-piece glass cell emulating the body of the ATOMSOURCE™. Similar absorbances were found for both devices, indicating that the hollow silica annulus is as efficient as the six jets at transporting sputtered atoms to the analysis volume.

A similar performance was found in analytical signal reproducibility for both atomizers however, the Delrin™ body of the ATOMSOURCE™ is a potential source for contamination by water [79]. Water vapor can have an appreciable deleterious effect on sputtering conditions in the glow discharge [75]. Water retention studies from introduced “wet” gas indicated that the ATOMSOURCE™ required a flushing period over 30 times that for GOUGH'S glass cell body to reduce water vapor in the cell to manageable levels. However, the design of the ATOMSOURCE™ is more robust than GOUGH'S cell which permits considerably higher power operation and therefore, greater sensitivity. The gain in sensitivity may be attenuated somewhat by a concomitant increase in background emission, but GOUGH et al. did not compare detection limits for the two atomizer designs.

Although both GOUGH'S cell and the ATOMSOURCE™ display similar analytical performance at similar operating conditions, the ATOMSOURCE™ design is more robust allowing a greater range and choice in operating conditions permitting the analyst more flexibility.

1.11 Scope of the Thesis

In this laboratory, we are primarily concerned with plasma emission methods due to its inherent advantages: simultaneous
multi-element analysis capability, large dynamic range, broad coverage of the periodic table, relative freedom from chemical interferences due to plasma dissociation of molecules and a cost which is significantly lower than mass spectrometric techniques which offer similar performance in many areas.

The ATOMSOURCE\textsuperscript{TM} was designed to achieve a maximum population of ground state atoms while minimizing atomic emission from excited states in the analysis volume [14]. The support gas flow is entrained away from the cathode surface before it reaches a T-shaped chamber which splits the flow producing a relatively long, thin cloud of ground state atoms sufficiently removed from the negative glow to prevent much excitation. This design is, of course, not optimum for atomic emission analyses.

Even with a less than optimum design however, KIM and PIEPMEIER reported a significant increase in atomic emission intensity with jet flow rate [69], although they did not report whether the power of the discharge was kept constant. Increasing the pressure of the discharge (by increasing the jet flow rate) tends to increase the power dissipated in the discharge which would increase sputtering rates [43] (although this would be attenuated by the pressure increase) and emission intensities [105]. This point may be moot however, since the increase in emission intensity with jet flow rate reported by PIEPMEIER et al. is primarily due to the drawing out of the negative glow from the jet assembly providing a greater plasma density in the analysis volume rather than to any reduction in re-deposition or increase in sputtering rate.
The demonstrated ability of the ATOMSOURCE™ to enhance the sample loss rates from cathode samples and the speculated reduction in preferential sputtering relative to static systems [69] provides cause for further investigation of the device. If these abilities are coupled with the inherent advantages available from using atomic emission detection, a superior glow discharge source may result. This thesis is concerned with the evolution and evaluation of a jet-assisted glow discharge source, which has been modelled on the ATOMSOURCE™ design although modifications have been made to provide optimum conditions for atomic emission detection.

Chapter 2 of this thesis is concerned with the original design for the jet-assisted glow discharge source and a preliminary investigation of its analytical performance. Chapter 3 presents a more in-depth analysis of how various parameter changes, including jet flow rate, pressure and power, effect sample loss rates and emission line intensities. Chapter 4 investigates the sputtering atomization processes that occur for three sources that use directed support gas flows to improve sampling efficiency, the GOUGH cell, the ATOMSOURCE™ and the jet-assisted glow discharge source. In addition, the burn spot is examined using scanning electron microscopy. Chapter 5 introduces some design modifications (lateral viewing of the jet-assisted plasma plume) that alleviate some of the problems associated with the original design. Atomic excitation is also examined in the plume. Chapter 6 compares the analytical performance of a GRIMM-type source and both a laterally viewed and axially viewed jet-assisted glow discharge source. Finally, Chapter 7 draws some conclusions from the presented work in the thesis and
suggests various design modifications which should result in a superior emission source.
CHAPTER 2

ORIGINAL DESIGN AND EVALUATION OF THE JET-ASSISTED
GLOW DISCHARGE ATOMIC EMISSION SOURCE

2.1 Preliminary Design Considerations

Since the ATOMSOURCE™ was designed for atomic absorption analyses, two principle modifications were made which made the design more compatible for atomic emission detection. Figure 1.6 illustrates the principal components that comprise the device: for a more comprehensive, detailed schematic, see OHLS [87]. The optical axis used in the ATOMSOURCE™ is sufficiently removed from the sample surface that emission from the negative glow is mostly obstructed. This is, of course, not optimum for atomic emission detection. Therefore, the optical axis has been rotated 90° in the jet-assisted glow discharge source so that the sample surface and complete negative glow can be viewed. This axial optical axis is more consistent with the GRIMM glow discharge (Fig. 1.3), a source used for atomic emission analyses.

The ATOMSOURCE™ relies on the manipulation of support gas flow rate through the jets to control the internal pressure inside the source. This design is too restrictive since it does not allow independent control of source pressure and jet flow rate. For a particular voltage applied to the electrodes, the current flow between them is largely dependent on the source pressure [18]. Pressure is, therefore, an important parameter that should be independently controllable. For this reason, the jet-assisted glow discharge has had
an auxiliary support gas inlet included in its design that allows the independent control of jet flow rate and source pressure.

These two aspects are the only significant departures from the ATOMSOURCE™ design. Other features, such as jet diameter, jet angle with respect to the surface normal and jet tip location from the sample surface conform to the original design so that the sputtering ability of the source has been preserved.

2.2 The Jet-assisted Glow Discharge Source

Figure 2.1 is a schematic diagram of the original jet-assisted glow discharge source design which contains expanded views of the anode-Macor™-sample interface region. As depicted in the schematic, significant cratering of the sample is evident where the jets impinge upon the surface as reported for the ATOMSOURCE™ [14, 69, 87]. This attests to the similarity between the two devices with regard to sputtering ability.

For the jet-assisted glow discharge, six jets, 1 mm² in cross-sectional area, are formed when square-shaped grooves, machined on the lower surface of the copper anode, are sealed by placing the anode onto the smooth finish of the Macor™ insulator. The jets are directed at the sample surface such that an angle of 60° is made with respect to the surface normal. As with the ATOMSOURCE™ [69], the jet tip is located 1 mm axially from the sample surface. Although a vacuum seal is not required between anode and Macor™, the anode is positioned firmly in place by three screws set into the Delrin™ flange. The vacuum seal in the anode-Macor™-sample interface is
Figure 2.1: Schematic representation of the jet-assisted glow discharge source. Adapted from [2].
maintained by o-rings between sample and Macor™ and Delrin™ and Macor™.

The Delrin™ flange, which allows the stainless steel body to achieve a floating positive potential, was necessary to confine the discharge to the interior of the anode. The quartz observation window was placed at the end of a 20 cm extension so that the optical axis is in line with the glow. The extension was necessary to impede vapor phase deposition of sputtered material on the surface of the window. Even with this extension in place, however, jet flow rates had to be maintained below 30 cL/min to avoid vapor phase deposition.

2.3 Peripheral Equipment

2.3.1 Support Gas Regulation and Metering

The source pressure was regulated using a brass needle-valve connected to the auxiliary support gas inlet, in conjunction with a VARIAN (Georgetown, Ont.) Model SD 90 floor pump (free air displacement of 5.4 m³/hr) and metered using a BALZERS (Hudson, NH) Model PKG 020 PIRANI thermocouple vacuum guage.

Flow rates of support gas supplied to the jets were measured using a MATHESON (Edmonton, Alta.) Model 7600 flow meter that was inverted so that the controlling valve was between the vacuum in the source and the flow tube (type 601).

2.3.2 Discharge Power Supply and Metering

Voltages were supplied to the jet assisted source through a 1500 ohm ballast resistor by a (1250 V, 500 mA max.) DC Power
Supply built by Electrical Services (Department of Chemistry, UBC). The ballast resistor ensured that the maximum current through the circuit never exceed 0.833 A. Electrical parameters reported were measured with FLUKE (Everett, WA) Model 77 multimeters.

2.3.3 Atomic Emission Detection

The monochromator used was a 0.35 meter GCA/MCPherson (Acton, MA) Model 270 CZERNY-TURNER with a 2400 line/mm holographic diffraction grating having peak efficiency at 500 nm. Light from the source was collected by a 90 mm focal length plano-convex lens and imaged 1:1 onto the entrance slit of the monochromator. A slit width of 50 μ was typically used.

The PMT detection system used consisted of a HAMMAMATSU (Middlesex, NJ) Model R955 photomultiplier tube mounted in a MCPherson/Schoeffel Model 654 PMT housing, a KEPCO (Flushing, NY) Model ABC 1500 power supply, and a KEITHLEY (Cleveland, OH) Model 427 current amplifier.

Emission signals were recorded after amplification using a HOUSTON INSTRUMENTS (Austin, TX) Model A5113-II Omniscribe recorder.

2.4 Sample Preparation and Weight Loss Measurements

Samples used were thin (1 mm) rectangles (7 x 11 cm) of commercial grade copper (99.9 % Cu) cleaned with a 2 % soap solution and an abrasive pad to remove the oxide layer, then dried with methanol. Sample loss rates were determined using the method reported by BOUMANS [18], where the weight of material removed
from the sample by sputtering, determined by before and after weight measurements, was divided by the lifetime of the discharge.

2.5 Analytical Evaluation of the Jet-assisted Glow Discharge Source for Atomic Emission Analyses

There are three variables in our system that can be directly manipulated to affect emission intensities: argon flow rate through the jets, pressure in the source, and the source voltage. While the jet flow rate and the pressure are independent variables which can be directly set, the anode-cathode voltage and current is a complex function of the pressure and jet flow rate. The product of the voltage and current is the power dissipated in the discharge.

Figure 2.2 is a contour plot which displays the variation of anode-cathode voltage as a function of jet flow rate and pressure. The source voltage was maintained at a constant value. KIM and PIEPMEIER [69] reported that the cell voltage for the ATOMSOURCE™ decreased as the jet flow rate was increased. The data in Fig. 2.2 indicate that the anode-cathode (cell) voltage decreases as the pressure increases, but is relatively constant as a function of jet flow rate at constant pressure. KIM and PIEPMEIER'S observations in which both pressure and jet flow rate were changing would be equivalent to measuring along a diagonal going from the lower left-hand corner to the upper right-hand corner of Fig. 2.2. The variation of current with pressure and jet flow rate is provided in Fig. 2.3. The current increases as the pressure increases but is relatively invariant with jet flow changes above 50 mL/min. From these two figures, it is apparent
Figure 2.2: Contour plot of the anode-cathode voltage as a function of metered source pressure and flow rate through the jets. Contours are labelled in units of volts.
Figure 2.3: Contour plot of the current as a function of metered source pressure and flow rate through the jets. Contours are labelled in units of mA.
that pressure and not jet flow rate is the important parameter which determines the voltage current characteristics of the source.

Figure 2.4 is a contour plot which displays the variation in power (the product of anode-cathode voltage and current) as a function of both pressure and jet flow rate. The power increases with an increase in pressure, but is, not surprisingly, largely unaffected by changes in jet flow rate at a constant pressure. The jet flow rate appears to have little effect in all three plots above a threshold of 80 mL/min; below this threshold, however, a drop in both anode-cathode voltage and current decreases the power of the discharge. Therefore, if emission intensities were measured at different jet flow rates and pressures, at a single source voltage, the results would be colored by the fact that there would be changes in the discharge power. Power dissipation in the discharge is an important parameter which determines emission intensities and sample loss rates. An increase in the power of the discharge was found to increase both sample loss rates and emission intensities at a constant jet flow rate and pressure (Fig. 2.5) so it seems reasonable that to obtain consistent results free from power fluctuations, one should keep the power of the discharge constant, by adjusting the voltage supplied to the electrodes, while varying the jet flow rate and pressure.

Figure 2.6 is a contour plot of Cu I emission intensity variation with jet flow rate and pressure inside the source at a constant power of 25 watts. As the pressure is increased, at a fixed jet flow rate, the emission intensity decreases; as the jet flow rate is increased at a fixed pressure, the emission intensity also decreases. The rate of decrease of emission intensity with an increase jet flow rate is larger
Figure 2.4: Contour plot of the discharge power as a function of metered source pressure and flow rate through the jets. Contours are labelled in units of Watts.
Figure 2.5: Cu I 324.75 nm emission intensity (○) and sample loss rate (■) vs. discharge power at a constant metered pressure of 2 mbar and a jet flow rate of 200 mL/min.
Figure 2.6: Contour plot of emission intensity of Cu I 324.75 nm as a function of metered source pressure and flow rate through the jets. Contours are labelled in relative units. Discharge power - 25 W.
at low pressures than at high pressure. If we consider the left-hand side of the contour map corresponding to zero jet flow rate as representative of the GRIMM design of glow discharge geometry, no noticeable enhancement of emission intensity is apparent in using the jet-assisted source over the GRIMM design at the same power.

In order to determine whether the reduction in emission intensity with jet flow rate was not an observation specific to Cu I 324.75 nm, the Cu II 224.70 nm response was similarly evaluated. Rather than reproduce a contour map of jet flow rates and pressures, a constant pressure of 3.7 mbar was maintained inside the source. This was a pressure at which emission intensities were at a maximum. The variation in Cu I and Cu II emission intensities as a function of jet flow rate at a fixed pressure and power is depicted in Fig. 2.7. Initially there is a sharp drop in Cu II emission intensity, followed by a levelling, then a gradual increase above about 50 mL/min.

This result can be possibly explained by differential pressures inside the source. The pressure is metered at a port on the side of the source body, but the pressure in the negative glow, approximately 1-2 mm from the cathode surface, is probably larger at the higher flow rates than that reported. These localized higher pressures should be accompanied by a larger density of argon ions and argon metastable ions. It is these argon metastable ions that cause the ionization and excitation of Cu II at 224.70 nm according to the equation:

\[
\text{Ar}^{m+} + \text{Cu}^0 \rightarrow \text{Ar}^0 + \text{Cu}^{+*} \quad [98]
\]
Figure 2.7: Cu I 324.75 nm emission intensity (○) and Cu II 224.70 nm emission intensity (■) vs. jet flow rate at a constant metered pressure of 2 mbar and discharge power of 25 Watts.
The energy available for the direct ionization and excitation of this line is the ionization potential of argon in addition to the energy difference between the metastable state and the ion ground state: \(15.76 + 0.18\) eV = 15.94 eV. The energy required to ionize and excite copper to emit at 224.70 nm is 7.73 eV + 8.23 eV = 15.96 eV. The slight energy defect of 0.02 eV can be accessed from the thermal motions of the argon ions. WAGATSUMA and HIROKAWA [112] reported that this line appeared very strongly in an argon plasma, but was weak in neon and not detected in nitrogen which strongly suggests a charge transfer mechanism.

The importance of independent control of both jet flow rate and pressure is evident in Figure 2.8. In this Figure, a single applied voltage on the discharge power supply was used and the metered pressure inside the source, and therefore the voltage-current characteristics of the discharge, were determined solely by jet flow rate. It is apparent that Cu I 324.75 nm emission intensity continually increases with increasing jet flow rate. The pressure in the source increases with each incremental increase in jet flow rate, however. This translates into increases in power as demonstrated in Figure 2.9 which, according to Fig. 2.5, translates into larger sample loss rates and emission intensities. Therefore, the increase in emission intensities evident in Fig. 2.8 are not brought about by jet flow rate increases, but rather by increases in pressure which translate into power increases.

In order to determine why copper emission intensities diminish with increase in jet flow rate at a constant pressure, the sample loss
Figure 2.8: Cu I 324.75 nm emission intensity vs. jet flow rate. Support gas flow through the jets determines the metered pressure and power.
Figure 2.9: Metered pressure (○) and discharge power (■) vs. jet flow rate. Support gas flow through the jets determines the metered pressure and power.
The rate was measured as a function of jet flow rate under similar conditions to that used in Fig. 2.7. The data plotted in Fig. 2.10 shows very little change in sample loss rate from 0 to 40 mL/min. Between 40 and 100 mL/min, the sample loss rate increases almost linearly with jet flow rate and thereafter begins to level off. This behavior is consistent with KIM and PIEPMEIER'S results using the ATOMSOURCE™ [69]. They demonstrated that sample loss rates were maximized at flow rates of approximately 200 mL/min for three different current densities.

Whether the tripling of sample loss rate is due to an increase in sputtering rate, the reduction in re-deposition of sputtered material back onto the cathode, or some combination of the two is not presently known. KIM and PIEPMEIER showed that the jets are able to erode small cone-like structures (caused from sample surface imperfections) found on sputtered areas using a design with no jets, so some degree of sputtering rate enhancement is possible, but the volume and number of the cones is not great enough to explain the large increase in sample loss rate from 40 to 90 mL/min seen in Fig 2.10.

How emission intensity relates to the sample loss rate is a matter of conjecture: one would assume that the greater the amount of material lost from the surface of the cathode, the greater the amount of atoms that can be excited in the negative glow and hence, the greater the emission intensity. Simple changes in jet flow rate without control over the power would lead one to believe that this is the case, since emission intensity increases with power (Fig. 2.5). However, the emission intensities for Cu I and Cu II demonstrate quite complex
Figure 2.10: Sample loss rate vs. jet flow rate at a constant metered pressure of 2 mbar and discharge power of 25 Watts.
behavior as a function of jet flow rate. It seems likely that the jets also cause a physical disruption of the glow discharge, perhaps making the negative glow more diffuse leading to a reduction in excitation ability. Some degree of visual proof of this speculation is apparent by the increase in size of the emission plume issuing from inside the hollow anode at larger jet flow rates. Since the anode is so close to the cathode, the formation of a positive column is not likely, therefore the plume should consist only of the negative glow.

2.6 Summary

The data presented in this Chapter indicates that although the use of jets in the present design enhances sample loss rates by more than a factor of three relative to a GRIMM-type glow discharge, there is an overall negative effect on Cu I and Cu II emission intensities when the experiment is carried out at a fixed pressure and power. The reasons for this phenomenon are purely speculative at this point. They include either an expansion (dilution) or cooling of the negative glow or some combination of the two which reduces the ability of the plasma to excite sputtered species when relatively large jet flow rates are used.
CHAPTER 3

INVESTIGATIONS OF POWER, JET FLOW RATE AND PRESSURE

3.1 Introduction

In the preceding chapter, the jets were shown to increase the amount of material removed from a copper cathode over a specific time period (sample loss rate) by a factor of three at a constant power and pressure, an effect supported in the literature [69]. However, the increased sample loss rate was not found to increase emission intensities for either Cu I or Cu II emission lines. In fact, the jets had an overall negative effect on the emission intensities at a constant power and pressure. It was speculated that this effect was probably due to an expansion and/or cooling of the negative glow upon application of the jets.

Detection of the electromagnetic radiation for the copper analyses with the jet-assisted source was performed with a monochromator and photomultiplier tube. This system can only provide sequential detection of emission signals and therefore cannot take advantage of the simultaneous nature possible with atomic emission methods. In comparing the Cu I and II signals, conditions in the glow discharge were similar but not identical.

In contrast, a linear photodiode array (LPDA) allows simultaneous detection of emission signals over a wavelength window of between approximately 1 to several decades of nanometers: choice depending on the required resolution. Additionally, the positioning of the wavelength window may be
changed simply by rotating the dispersion grating providing greater flexibility relative to a conventional direct reading polychromator.

In this Chapter, our study is extended to include stainless steels as cathodes using a 2048 diode LPDA detection system for the additional characterization of the jet-assisted glow discharge source to determine whether the observations and conclusions made with copper as a cathode were representative of other sample types and emission lines.

3.2. Experimental

3.2.1 Equipment

The jet-assisted source has been previously described [2] although some modifications have been made to the source (see Fig. 3.1): optical ports have been added to the side walls of the source to permit side-on or lateral-viewing of the negative glow.

The inverted flow meter used previously to control and measure the flow of support gas through the jets was replaced by a Sierra Instruments (Carmel Valley, CA) Model 840 mass flow controller calibrated for argon gas at flow rates between 0 and 1 SLPM. The mass flow controller allows the jet flow rate to be controlled with more accuracy and with a greater precision (quoted accuracy: ±0.9 % of full scale; quoted reproducibility: ±0.5 % of full scale).

The floor pump used to evacuate the source was upgraded to a Balzers (Hudson, NH) Model Duo-016B rotary vane vacuum pump with a volume flow rate of 16 m³/hr allowing the source to be evacuated to below 10⁻³ mbar before the introduction of support gas.
Figure 3.1: Jet-assisted glow discharge source with side optical ports
This was effective in reducing molecular emission from residual air as evidenced by monitoring the N-H bandhead at 337.1 nm.

A Schoeffel-McPherson (Acton, MA) Model 2061, 1-m CZERNY-TURNER monochromator incorporating a SCHOEFFEL-MCPHERSON Model AH-3264, 120x140 mm, holographic grating with 1200 lines/mm was used. The reciprocal linear dispersion of the spectrometer is 0.833 nm/mm. Detection was achieved using a Reticon (Sunnyvale, CA) RL2048S Linear Photodiode Array (LPDA). The LPDA system consisted of the 2048 element LPDA which has a light sensing area of 0.5 mm in height by 51.2 mm in length. The pixels are 12 µm wide mounted on 25 µm centers. The spectrometer provided a spectral bandwidth of 0.057 nm expressed as full width at half maximum (FWHM) using an entrance slit width of 65 µm.

The LPDA was controlled by a RC1021 satellite board which contained a slot allowing the interfacing of a Melcor (Trenton, NJ) Model CPL4-71-10L thermoelectric (PELTIER) cooler. The use of the PELTIER cooler reduced the thermal emission of electrons in the diode array circuits which reduced the dark current signal in the LPDA. This allowed the use of longer integration times for data acquisition which was found to be necessary for the relatively weak (cf. the inductively coupled plasma) glow discharge plasma. To prevent ice from forming on the protective covering of the LPDA, a steady stream of nitrogen gas was passed over the face of the array when the PELTIER cooler was in operation. LPDA readout was accomplished using a 1 MHz, 12 bit analog-to-digital converter card which plugged into the Telex (Tulsa, OK) Model 1280 IBM AT
compatible computer. The Telex contained 1 MByte of RAM, a 20 MByte hard disk drive and dual floppy drives.

Relative line shapes of Cu I 222.78 and 324.75 nm lines were obtained using a Leco Instruments Model PDA-10A Plasmarray Spectrometer (Mississauga, Ont) as the Schoeffel-McPherson 1-m spectrometer provided insufficient resolution. The Leco spectrometer is composed of three optical systems: a preselection polychromator to filter out unwanted radiation, a second grating to recombine the previously dispersed light to form a quasi-white beam which is subsequently dispersed by a high resolution echelle grating, onto a photodiode array. The overall system allows wide wavelength coverage in conjunction with high resolution. The Leco spectrometer has been characterized in other publications [25, 68, 76, 83]. For the Cu I resonance line at 324.75 nm, the reciprocal dispersion was found to be 2.37 pm/pixel and the spectral bandwidth, 9.7 pm [76]. The Cu I resonance line was chosen since it demonstrated definite line shape changes with increasing jet flow rate and explains the Cu I emission intensity behavior with increasing jet flow rate found in the previous Chapter.

3.2.2 Samples

Calibration curves for Ni were obtained using NBS steel samples c1151, 1155, 1286, c1288 and 1761. Emission intensity and sample loss rate measurements were made with 304-type steel. Emission line shapes were evaluated with commercial grade copper (99.9%). All samples were prepared and sample loss rates
determined according to the procedures outlined in the previous Chapter.

3.3. Results

3.3.1 Jet Flow Rate Effect on other Emission Lines

Figures 3.2a and 3.2b are 2048 diode array spectra of NBS 1155 steel from 356 to 374 nm at similar conditions with the exception of argon flow rate through the jets: Fig. 3.2a corresponds to a flow of 0 cL/min; Fig. 3.2b to 30 cL/min. The 30 cL/min case demonstrates a markedly more complex spectrum with a more active baseline relative to the 0 cL/min flow rate case. On further comparison of these spectra, it is apparent that some emission lines are increased in intensity by the application of the jets, a feature contradictory to the behavior found for copper; some are weakened, an effect in agreement with the copper analysis; and some are unaffected, notably support gas emission lines.

From Table II it is apparent that emission lines with lower energy levels (LEL) which terminate at or near the ground state suffer from a reduction in emission intensity with the application of the jets, the extent of reduction being dependant on the oscillator strength of that particular line. Conversely, emission lines with LEL relatively removed from the ground state (but still having upper energy levels sufficiently close to the ground state to enable excitation in the glow discharge) have emission intensities that are enhanced by an increase in jet flow rate. For example, the Fe I resonance line at 371.99 nm is reduced by a factor of 2 by increasing the jet flow rate
Figure 3.2: 2048 diode array spectra of an NBS 1155 stainless steel sample at a power of 30 W and a pressure of 9 mbar. Jet flow rate: a) 0 cL/min; b) 30 cL/min.
Table II: Some fundamental characteristics of designated emission lines from Fig. 3.2

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>WAVELENGTH (nm)</th>
<th>LOWER ENERGY LEVEL (eV)* [67]</th>
<th>UPPER ENERGY LEVEL (eV)* [67]</th>
<th>OSCILLATOR STRENGTH [67]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe I</td>
<td>357.01</td>
<td>0.91</td>
<td>4.39</td>
<td>0.129</td>
</tr>
<tr>
<td>Ar II</td>
<td>358.84</td>
<td>19.49</td>
<td>22.95</td>
<td>--</td>
</tr>
<tr>
<td>Cr I</td>
<td>359.35</td>
<td>0</td>
<td>3.45</td>
<td>0.291</td>
</tr>
<tr>
<td>Cr I</td>
<td>360.53</td>
<td>0</td>
<td>3.44</td>
<td>0.316</td>
</tr>
<tr>
<td>Fe I</td>
<td>360.89</td>
<td>1.01</td>
<td>4.45</td>
<td>0.159</td>
</tr>
<tr>
<td>Fe I</td>
<td>371.99</td>
<td>0</td>
<td>3.33</td>
<td>0.0338</td>
</tr>
<tr>
<td>Fe I</td>
<td>373.49</td>
<td>0.86</td>
<td>4.18</td>
<td>0.189</td>
</tr>
<tr>
<td>Fe I</td>
<td>373.71</td>
<td>0.05</td>
<td>3.37</td>
<td>0.0297</td>
</tr>
</tbody>
</table>

* energy levels relative to atomic ground state
from 0 to 30 cL/min; Fe I 357.01 nm is enhanced by more than a factor of 2.5; and yet Fe I 373.49 nm is only enhanced by a factor of approximately 1.5.

It is unlikely that this behavior is due to a temperature change with variation of flow rate through the jets as emission intensity changes would be in the same direction for the lines in question. That is to say each of the lines would be enhanced by an increase in temperature or reduced for a temperature drop. It seems likely that this behavior stems from a self-absorption problem which is either initiated or intensified by the flow of support gas through the jets.

3.3.2 Evidence for Self-absorption

If an emission line suffers from self-absorption, it tends to possess a flatter, broader line shape since absorption is strongest at the line center [19]. This appears to be the case with Cu I 324.75 nm. In Figs 3.3a and 3.3b, depicting the Cu I resonance line at 3.7 and 9 mbar respectively, the relative line shapes are both flattened and broadened by increasing the flow rate through the jets from 0 to 30 cL/min. The broadening is not brought about by pressure effects as the relative line shapes of the emission line shown in Fig. 3.3c at 3.7 and 9 mbar, both at the same flow rate, are the same. This broadening is not apparent for Cu I 222.78 nm, as seen in Fig. 3.3d representing a pressure of 3.7 mbar. Both relative line shapes appear identical and the emission line intensity is enhanced by increasing the flow rate from 0 to 30 cL/min. At 9 mbar (Fig. 3e), however, the line intensity is somewhat reduced and the line shape broadened by
Cu I 324.75 nm emission line shape changes with jet flow rate and pressure at a power of 30 W. a) 3.7 mbar: (○) - (cL/min, (●) - 30 cL/min; b) 9 mbar: (○) - 0 cL/min, (●) - 30 cL/min; c) 0 cL/min: (○) - 3.7 mbar, (●) - 9 mbar.
Figure 3.3 (cont): Cu I 222.78 nm emission line shape changes with jet flow rate and pressure at a power of 30 W. a) 3.7 mbar: (○) - 0 cL/min, (■) - 30 cL/min; b) 9 mbar: (○) - 0 cL/min, (■) - 30 cL/min.
increasing the flow rate through the jets indicating the onset of self-absorption.

Further evidence of a self-absorption problem induced by the jets is found in Figs 3.4 and 3.5. Figure 3.4 shows calibration curves for Ni I 352.45 nm at a zero and 30 cL/min flow rate through the jets. Although this line is not a resonance line, its LEL is close enough to the ground state that a substantial proportion of Ni atoms in the glow reside at this energy level (see Table III). The zero flow rate case displays adequate linearity for use as a calibration curve. The 30 cL/min case exhibits marginally enhanced signals at low Ni concentrations relative to the zero flow rate case, but increasingly reduced signals at greater Ni concentrations. Figure 3.5 demonstrates calibration curves of two Ni I line selections, 352.45 and 361.95 nm, both with a flow rate of 25 cL/min through the jets. The calibration curve for Ni I 352.45 nm shows roll-over at high Ni concentrations indicative of self-absorption, but the weaker line selection with a relatively larger LEL (Table III) displays linear behavior.

3.3.3 Evaluation of Absorption Coefficients

Self-absorption describes the absorption of photon emission by atoms of the same type as the emitters. In the self-absorption process, the atom must initially reside in the lower energy level of the transition in question, usually the ground state or other well-populated lower level. Once the photon is absorbed, it may be re-emitted, but the excited state can also be depopulated by collisions therefore reducing the intensity of that particular radiation [19]. The extent to
Figure 3.4: Calibration curves of Ni I 352.45 nm at a power of 35 W and pressure of 9 mbar at a jet flow rate of 0 cL/min (○) and 30 cL/min (■).
Figure 3.5: Calibration curves of Ni I 352.45 nm (○) and Ni I 361.94 nm (■) at a power of 35 W, pressure of 9 mbar and a jet flow rate of 25 cL/min.
Table III: Some fundamental characteristics of Nickel I emission lines from Figs 3.4 and 3.5

<table>
<thead>
<tr>
<th>WAVELENGTH (nm)</th>
<th>LOWER ENERGY LEVEL (eV)* [67]</th>
<th>UPPER ENERGY LEVEL (eV)* [67]</th>
<th>OSCILLATOR STRENGTH [67]</th>
</tr>
</thead>
<tbody>
<tr>
<td>352.45</td>
<td>0.03</td>
<td>3.54</td>
<td>0.121</td>
</tr>
<tr>
<td>361.94</td>
<td>0.42</td>
<td>3.85</td>
<td>0.300</td>
</tr>
</tbody>
</table>

* energy levels relative to ground state
which a given line is susceptible to self-absorption can be evaluated using the BEER-LAMBERT law:

\[ l = l_0 e^{-k_\lambda l} \]  \hspace{1cm} (3.1)

where \( k_\lambda \) is the absorption coefficient and \( l \) is the absorption path length. For a given set of conditions (constant \( l \)), \( k_\lambda \) may be used to quantify the relative likelihood a transition has of absorbing its own radiation. According to FERREIRA and HUMAN, the absorption coefficient at the center of a line profile, \( k_0 \), can be described by the relationship:

\[ k_0 = \frac{\pi^{1/2} e^2 \lambda^2}{mc^2 \Delta \lambda_D} nf \]  \hspace{1cm} (3.2)

or, with substitution of constants:

\[ k_0 = 5.04 \times 10^{-13} \frac{\lambda^2}{\Delta \lambda_D} nf \]  \hspace{1cm} (3.3)

where \( \lambda_0 \) is the wavelength of the line center, \( \Delta \lambda_D \) the DOPPLER width of the emission line, \( n \) the number density of atoms capable of absorbing radiation at \( \lambda_0 \), and \( f \) the oscillator strength of the transition [49].

The values of the DOPPLER widths used here, calculated by the method outlined by FERREIRA and HUMAN, are based on a DOPPLER temperature of 1100 K, a reasonable estimate for a GRIMM glow discharge obtained from the literature [50]. All number densities have
been calculated relative to the Fe I ground state by assuming that a BOLTZMANN distribution exists such that:

\[
\frac{n_p}{n_o} = \frac{g_p}{g_o} e^{-E_p/kT}
\]

where subscript "p" refers to the LEL of the transition in question and subscript "o" to the Fe I ground state. Glow discharges are not in thermodynamic equilibrium [22], and therefore can not be characterized by a single temperature. Excitation temperatures, necessary for the determination of BOLTZMANN distributions, are typically greater than DOPPLER temperatures in a glow discharge. BÜGER and EL ALFY reported Fe I temperatures of approximately 3000 K for resonance lines and lines with a LEL of 0.86 eV in a GRIMM glow discharge [27]. When dealing with elements other than Fe, both their concentration in the sample and sputter yield [12] relative to Fe were taken into account. In addition, excitation temperatures were assumed to be similar to that for Fe I.

Absorption coefficients for some of the emission lines studied corresponding to the 0 cL/min jet flow rate case (emulating a GRIMM glow discharge) are presented in Table IV. It should be noted here that caution must be exercised in the direct comparison of absorption coefficients to explain relative effects on emission intensity as it is apparent from the BEER-LAMBERT law that the absorption coefficient occurs in the exponent. The intent is to qualitatively explain which lines are more likely to suffer from self-absorption by the calculation and tabulation of absorption coefficients at a 0 cL/min jet
Table IV: Absorption coefficients of some emission lines studied and their general intensity change with an increase of jet flow rate from 0 to 30 cL/min.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
<th>Absorption coefficient (cm² x 10³)</th>
<th>General intensity change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe I</td>
<td>360.89</td>
<td>0.06</td>
<td>Increase</td>
</tr>
<tr>
<td>Fe I</td>
<td>357.01</td>
<td>0.21</td>
<td>Increase</td>
</tr>
<tr>
<td>Fe I</td>
<td>373.49</td>
<td>0.49</td>
<td>Increase</td>
</tr>
<tr>
<td>Fe I</td>
<td>373.71</td>
<td>1.1</td>
<td>Decrease</td>
</tr>
<tr>
<td>Fe I</td>
<td>371.99</td>
<td>2.0</td>
<td>Decrease</td>
</tr>
<tr>
<td>Cr I</td>
<td>359.35</td>
<td>4.8</td>
<td>Decrease</td>
</tr>
<tr>
<td>Cr I</td>
<td>360.53</td>
<td>5.2</td>
<td>Decrease</td>
</tr>
<tr>
<td>Cu I</td>
<td>324.75</td>
<td>18</td>
<td>Decrease</td>
</tr>
</tbody>
</table>
flow rate. From the table it is apparent that lines with relatively large absorption coefficients suffered from emission intensity reversal in Fig. 3.2b relative to Fig. 3.2a. In particular, the Cu I 324.75 nm resonance line is characterized by a $k_0$ almost an order of magnitude greater than that of the Fe I 371.99 nm resonance line. Conversely, lines with relatively small absorption coefficients did not significantly suffer from self-absorption and their emission intensities were increased by the increase in sample loss rate brought about by an increase in jet flow rate.

3.3.4 Models for Self-absorption in the Jet-assisted Glow Discharge

In a previous study [2], it was shown that sample loss rates (SLR) can be increased by up to a factor of three in increasing the flow rate through the jets from 0 to 20 cL/min, therefore the self-absorption problem, apparent with a large increase in support gas flow through the jets, is presumably brought about by an increase in the amount of material removed from the sample surface. A simple model may be used to describe this behavior. Since most sample atoms in the negative glow reside in the ground state [49], any increase in the amount of sputtered atoms reaching the negative glow could initiate or intensify a self-absorption problem. Other parameters have the ability to affect sputtering rates. The previous study indicated that power increases caused a near linear increase in SLR; DOGAN et al. demonstrated that the sputtering rate was inversely proportional to the root of the internal pressure of the source over a limited range of pressures typically used for analysis [39]. Therefore, for the simple model to be valid, increases in SLR brought about by
these parameter changes should also initiate or intensify the self-absorption problem. However, as these analyses were done with cathodes other than stainless steel or sources other than the jet-assisted source, verification of these trends is prudent.

Figures 3.6a and 3.6b represent SLR variation with power and flow rate through the jets at 9 and 3.7 mbar respectively. The SLR behavior of 304 steel was found to be consistent with past evidence and with the findings of DOGAN et al.: power increases produce a near-linear response in SLR; flow rate increases initially produce an increase in SLR followed by a gradual levelling off at higher flow rates; and a pressure drop results in an increase in SLR. Therefore, if the self-absorption problem results from a simple increase in sputtered material reaching the negative glow as proposed by the simple model outlined above, one would expect similar behavior with an increase in power and drop in pressure to that found with an increase in flow rate through the jets.

This is not the case, however. Figures 3.7a and 3.7b illustrate emission intensity variation with power and flow rate through the jets at 9 mbar for Fe I 357.01 nm and Fe I 371.99 nm, respectively. Both show behavior consistent with the diode array spectra in Figs. 3.2a and 3.2b: Fe I 357.01 nm is enhanced and the resonance line at 371.99 nm is reduced by the application of the jets at any selected power. However, each display a near-linear increase in emission intensity with a power increase. Figures 3.8a and 3.8b represent the same two emission lines and parameter changes except at a pressure of 3.7 mbar. These demonstrate a similar response to power changes to that found at 9 mbar, but the response to flow rate
Figure 3.6: Contour plots of sample loss rate for steel as a function of power and jet flow rate at two pressures: a) 9 mbar; b) 3.7 mbar. Contours in units of μg/sec.
Figure 3.7: Contour plots of Fe I emission intensity at 9 mbar pressure as a function of power and jet flow rate: a) 357.01 nm; b) 371.99 nm. Contour units: a.u.
Figure 3.8: Contour plots of Fe I emission intensity at 3.7 mbar pressure as a function of power and jet flow rate: a) 357.01 nm; b) 371.99 nm. Contour units: a.u.
changes appears to be more complex. Of more significance, however, is the apparent decrease in emission intensity displayed by both lines with the pressure drop despite the increase in SLR.

In summary, the three parameters that effect SLR, power, pressure and flow rate through the jets, each produce different emission intensity behavior refuting the simple model for the self-absorption problem. The action of the jets appears to be the only mechanism that causes the self-absorption evident in the emission spectra.

WEST and HUMAN, investigating self-absorption in a GRIMM glow discharge, assumed a two layer model for the light source [115]. In this model, the first layer represented the plasma or negative glow which contained uniformly dispersed emitting and absorbing atoms; the second layer surrounded the glow and consisted entirely of absorbing atoms. Therefore, any emission from layer 1 had to pass through layer 2 where significant absorption may take place before detection. The extent of absorption by layer 2 was dependent on the absorption coefficient for the particular emission line in question and the width of layer 2. From the previous study with copper as a cathode it was noted that the jets caused a physical disruption of the negative glow (layer 1 in the model) causing it to be lengthened along the optical axis. This disruption also occurred using stainless steel as a cathode: Fig. 3.9 shows the plume viewed side-on through an optical port on the side of the jet-assisted source at a height of approximately 40 mm above the cathode surface at flow rates of 10 and 30 cL/min and pressures of 3.7 and 9 mbar. It is apparent that the plume is less restricted at the lower pressure, the visible emission
Photographs of the discharge taken through the side optical port of the jet-assisted glow discharge source at a power of 40 W using a stainless steel cathode. a) 3.7 mbar, 10 cL/min; b) 3.7 mbar, 30 cL/min; c) 9 mbar, 10 cL/min; d) 9 mbar, 30 cL/min.

Figure 3.9:
extends the length of the port, whereas at 9 mbar the plume is more confined inside the hollow cone-shaped anode. If layer 1 is lengthened by the jets, then one would surmise that layer 2 may also be extended along the optical axis by the use of the jets. This lengthening of layer 2 coupled with an increase in absorption coefficient brought about by the increase in sample loss rate may provide an explanation for the self-absorption problem.

Absorbance and emission measurements taken through the side port can be used to quantify the lengthening of the two layers; however, as the jets also act to increase SLR, these measurements must be first corrected before any true indication of lengthening of the layers is obtained. Table V lists absorbance and emission measurements taken at 3.7 mbar and 30 Watts, 9 mbar and 40 Watts, and at 2 heights above the sample (cathode) surface for a number of flow rates through the jets. SLR at the two pressures and powers is additionally listed for correction purposes.

Owing to the fact that layer 2 presumably contains no emitting atoms, the lengthening of layer 1 by the application of the jets can be easily verified by examining emission intensities corrected for increases in SLR. The lengthening of layer 2 is more difficult to ascertain, however, since both layers contain absorbing atoms and the demarcation between layers is unclear. However, a qualitative impression of the extent of layer 2's presence can be made relative to layer 1 by examining both absorbance and emission measurements, each corrected for SLR increases: for example, at a given set of conditions, a large absorbance coupled with a small emission signal suggests layer 2 is being sampled.
Table V: Effect of jet flow rate on the sample loss rate at two source pressures and on Fe I 371.99 nm absorbance and emission intensity at two source pressures and heights above the cathode surface.

<table>
<thead>
<tr>
<th>Flow Rate (cL/min)</th>
<th>SLR (μg/sec)</th>
<th>3.7 mbar</th>
<th>9 mbar</th>
<th>3.7 mbar</th>
<th>9 mbar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35 mm</td>
<td>55 mm</td>
<td>35 mm</td>
<td>55 mm</td>
<td>35 mm</td>
</tr>
<tr>
<td>0</td>
<td>5.0</td>
<td>5.0</td>
<td>0.021</td>
<td>0.000</td>
<td>0.059</td>
</tr>
<tr>
<td>5</td>
<td>7.1</td>
<td>5.5</td>
<td>0.188</td>
<td>0.033</td>
<td>0.136</td>
</tr>
<tr>
<td>10</td>
<td>8.5</td>
<td>6.25</td>
<td>0.423</td>
<td>0.186</td>
<td>0.189</td>
</tr>
<tr>
<td>15</td>
<td>9.4</td>
<td>7.6</td>
<td>0.920</td>
<td>0.504</td>
<td>0.297</td>
</tr>
<tr>
<td>20</td>
<td>10.05</td>
<td>9.1</td>
<td>1.191</td>
<td>0.936</td>
<td>0.390</td>
</tr>
<tr>
<td>30</td>
<td>11.5</td>
<td>11.5</td>
<td>1.253</td>
<td>1.006</td>
<td>1.146</td>
</tr>
</tbody>
</table>
Figures 3.10a and 3.10b illustrate the absorbance and emission measurements listed in Table V corrected for SLR changes and plotted against argon flow rate through the jets at 35 and 55 mm above the sample surface respectively. From Fig. 3.10a, representing the 35 mm case, the lengthening of layer 1 at 3.7 mbar is apparent from the large increases in Emission/SLR with flow rate; however, at 4 mbar, layer 1 is relatively confined to the sample surface as Emission/SLR increases only marginally, even at high flow rates. Absorbance/SLR at 3.7 mbar increases dramatically until 20 cL/min where the response levels off, indicating that the number density of absorbers has reached a constant. This, coupled with the Emission/SLR response, suggests that at 35 mm above the sample and at 3.7 mbar, layer 2 is gradually being replaced by layer 1 at flow rates greater than 20 cL/min. This replacement is not evident at 9 mbar as the Absorbance/SLR continually increases with flow rate while the Emission/SLR response is hardly effected. This behavior at the higher pressure indicates a growth of layer 2 only at 35 mm above the sample. At 55 mm above the sample (Fig. 3.10b), Absorbance/SLR behavior is similar, although somewhat reduced, at both pressures to that found at 35 mm; however, small Emission/SLR signals over the range of flow rates investigated indicates that layer 1's presence is marginal at 55 mm. Therefore at this height above the sample, layer 2 becomes dominant.

From the spectroscopic measurements taken at the two heights above the sample it is apparent that at 3.7 mbar and 30 watts, absorbance is maximized relative to emission at a flow rate through the jets of between 15 to 20 cL/min. This suggests that at this
Figure 3.10: Side-viewed spectroscopic measurements for Fe I 371.9 nm as a function of jet flow rate. The signals have been normalized for SLR increases. Viewing height above the sample: a) 35 mm; b) 55 mm. Absorbance: 3.7 mbar (○), 9 mbar (●); Emission: 3.7 mbar (◇), 9 mbar (■).
pressure and range of flow rates, photons from layer 1 would have the largest probability of being absorbed and contributing to the self-absorption problem. This is reflected in the Fe I 371.99 nm emission intensity contour plot in Fig. 3.8b where the maximum reduction in the signal occurs over the stated range of jet flow rates. At jet flow rates greater than 20 cL/min, absorbance remains relatively constant, but emission intensity increases dramatically indicating a replacement of layer 2 with layer 1. Therefore one would expect the self-absorption problem to be alleviated somewhat at jet flow rates greater than 20 cL/min. This also correlates with Fig. 3.8b since the rate at which the Fe I emission line intensity is reduced with jet flow rate is in turn reduced. At 9 mbar and 40 Watts, layer 1 is more confined to the sample surface allowing layer 2 to predominate and be maximized at the largest flow rate investigated. This suggests that at this pressure, the self-absorption problem should be exacerbated with increasing jet flow rate. This correlates well with the Fe I resonance line emission intensity contour plot at 9 mbar depicted in Fig. 3.7b where the maximum reduction in the signal occurs at the largest jet flow rate investigated.

3.4. Summary

Although support gas flows through the jets increase the sample loss rate of both copper and stainless steels, the emission intensities of some investigated spectral lines were subject to a reduction in signal. Evidence presented in this thesis indicates that this effect does not originate from a simple increase in sputtered material but from a directional flow induced by the application of the
jets which acts to entrain sputtered atoms along the optical axis of the source. As sputtered atoms in and beyond the negative glow typically reside in the ground state, the entraining by the jets increases the absorption path length for axial (end-on) detection. This leads to the self-absorption of emission lines with lower energy levels near the ground state and therefore well populated in the plasma. This is a particularly unfortunate occurrence as resonance lines are typically the most sensitive lines available in the glow discharge and therefore the most suitable selection for quantitative analyses.
CHAPTER 4

INVESTIGATION OF DIRECTED SUPPORT GAS FLOWS FOR THE
IMPROVEMENT OF SAMPLING EFFICIENCY IN GLOW
DISCHARGES

4.1 Introduction

4.1.1 Re-deposition

Although the low pressure glow discharge is a useful source for
analytical atomic spectrometry, it has been shown in Chapter 1 that
the source suffers from some problems. Chief among these is the re-
deposition of sputtered atoms back onto the surface of the sample.
FERREIRA and BÜGER have reported that re-deposition is primarily
cau sed by four processes [48]:

1. A portion of sputtered atoms are back-scattered by initial
collisions onto the cathode surface.

2. Although cathode atoms are ejected from the surface with
appreciable kinetic energy, their motion is rapidly slowed by
collisions with support gas atoms. The thermalization of
sputtered species is so rapid that transport to the negative glow
is primarily governed by diffusion. Therefore, although the
concentration gradient of sputtered species enhances transport
to the negative glow, the overwhelming relative population of
support gas atoms ensures that a significant proportion of
sputtered species will diffuse back onto the cathode surface.
3. For most glow discharge devices, support gas is introduced toward the cathode which would impede sputtered species transport to the negative glow and contribute to re-deposition.

4. A portion of sputtered species is ejected from the cathode as positive ions, which would be returned to the cathode surface by the electric field.

It has been shown that the four processes combined can re-deposit up to 90% of the sputtered atoms onto the surface of the cathode at 0.1 torr [61]. This pressure is an order of magnitude less than those typically used in analytical glow discharges. One would expect that the higher pressure operation would increase the amount of back-scattering and enhance the directional flow of support gas towards the cathode. It would also reduce the mean free path of sputtered atoms causing them to be thermalized closer to the cathode, therefore increasing the probability of atoms diffusing to the cathode. However, higher pressure operation would typically require lower voltages and provide more collisions for impacting ions before they strike the surface; therefore one would expect the impacting ions at the higher pressure to possess less energy and the likelihood of producing a sputtered ion would be reduced. According to MASE et al., at pressures typically used for analytical applications, diffusion is the principal agent for re-deposition [82]; therefore, one would expect that the higher pressure operation would result in an even greater proportion of sputtered atoms re-depositing on the cathode surface than that reported for a 0.1 torr discharge.

This expectation is born out by a simple calculation of sputtered atom re-deposition by HARRISON who reported a figure of 94% for a
hemispherical cathode [24]. This value was obtained by calculation of the uncorrected sputtering ratio according to BOUMANS [18], followed by comparison to a literature value for a 200 eV impacting argon ion.

The GRIMM-type glow discharge is associated with low redeposition through the use of an additional vacuum port near the cathode surface [48]. The majority of atoms which escape redeposition, however, are still lost to the system before they can be excited in the negative glow. Therefore, a process is needed whereby the re-deposition process is impeded, and transportation of sputtered species to the negative glow is aided. This would significantly increase the atomization efficiency of the glow discharge.

4.1.2 Directed Support Gas Flows

As indicated in Chapter 1, two glow discharge atomizers have been constructed in the past which use directed support gas flows for the improvement of sampling efficiency. GOUGH used a flow of support gas parallel to the sample surface to impede re-deposition [54]. Analyte Corporation's ATOMSOURCE™ used a flow of support gas which impinges upon the sample surface [14]. The existence of craters on the burn spot where the jets point indicates that some enhancement of sputtering rate at that point is possible.

The jet-assisted glow discharge source uses a similar design to the ATOMSOURCE™, therefore it is expected that jet effects found for the jet-assisted source would also be representative of the ATOMSOURCE™. This belief has been verified to some extent in the past since a similar pattern of craters on the sample surface and increases in sample weight loss relative to a static gas flow discharge
were evident after sputtering [2, 3] indicating that atomization processes occurring with the ATOMSOURCE™ were also present in our jet-assisted source.

The intent of this Chapter is to evaluate the re-deposition processes of directed gas flow sources and in particular, the jet-assisted source with the aid of Scanning Electron Microscopy and Energy Dispersive X-ray Fluorescence and compare the results to other glow discharge sources.

4.2. Experimental

4.2.1 The Jet-assisted Glow Discharge Source

The jet-assisted glow discharge source has been described elsewhere [2, 3] although some modifications where made to the vacuum system. The End-on view window was replaced by a flange which allowed the orifice to be used as a pumping port. It was found that the inclusion of this vacuum port produced a less turbulent jet flow. The side vacuum port was not used. In addition, the thermocouple vacuum gauge was replaced with a Varian (Lexington, MA) Model 815 thermocouple gauge controller.

4.2.2 Scanning Electron Microscopy and Energy-dispersive X-ray Analysis

Two Scanning Electron Microscopes (SEM) were used: a Hitachi (Tokyo, Japan) Model S-570 was used in conjunction with Energy-Dispersive X-ray Analysis (EDX); the Model S-2300 was used when no EDX analysis was required. Images from both SEMs were
obtained through secondary electron detection. The EDX detector, maintained at 77 K by liquid nitrogen-cooling, was connected to a Kevex 8000 II computer system used for data evaluation.

4.2.3 Sample Re-deposition Holder

A sample holder was constructed to secure two sections of cathode together to form a vacuum seal, allowing each to be sputtered at the same time (see Fig. 4.1). For this particular experiment, copper and brass cathodes were used. Re-deposition could be evaluated by examining the copper cathode for traces of zinc. The analysis of burn spots using this sample holder requires a careful selection in the pair of cathodes. Sputtering rates and secondary electron coefficients should be similar for the two cathodes to ensure that some degree of discharge homogeneity occurs over the whole burn spot. The brass chosen for these experiments contained 71 % copper and 29 % zinc. Boumans [18] found that brass of composition 64.4 % copper and 35.6 % zinc had a sputtering rate approximately 25 % higher than copper and a BOUMANS' parameter, Vo, presumably related to the secondary electron coefficient, about 5 % higher than copper. These differences should be reduced using a higher copper content brass, as in this case.

However, analysis of the burn spot area subjected to sputtering for re-deposition using this sample holder yielded irreproducible results: using the SEM, it was found that most sputtering, especially at low jet flow rates, was localized in the gap between cathodes. This localization may be due to a hollow cathode effect at the junction of the two cathodes which would be increased with time as the gap is
Figure 4.1: Sample holder used to compress two individual cathodes to form a single cathode that can be used to form a vacuum seal.
widened by sputtering. The analysis of edge re-deposition, however, which underwent no sputtering, should not be unduly effected.

4.2.4 Sample Preparation

Sample preparation of copper cathodes was carried out as follows except where indicated. Before being exposed to sputtering, each surface was abraded using 320 grit Durite®, a silicon-carbide abrasive paper, to remove the oxide layer from the copper surface. The surface was then washed in water, dried in methanol and finally polished with a methanol-soaked cotton-tipped applicator.

4.3. Re-deposition in Directed Support Gas Flow Sources other than the Jet-assisted Glow Discharge Source

4.3.1 GOUGH'S Sputtering Cell

The extent to which GOUGH'S cell reduces re-deposition is difficult to determine. Certainly, the barrier provided by a tangential gas flow would be effective in preventing the re-deposition of atoms ejected beyond the gas stream, but it would be ineffective in preventing the return of sputtered ions and may produce more back-scattering. However, these processes are small components contributing to the re-deposition phenomenon as attested by the findings of MASE [82]. The extent of re-deposition is essentially determined by where the transport processes of the discharge become diffusion controlled: if this occurs closer to the sample surface than 0.5 mm (the distance measured between the sample surface and the hollow annulus gap), then presumably the stream of
gas would be ineffective in reducing re-deposition. Therefore, to significantly reduce diffusion back to the cathode surface, sputtered atoms should be ejected with sufficient energy to prevent thermalization before they have travelled axially 0.5 mm into the discharge.

According to VON ENGELE, the mean free path of argon atoms at a pressure of 1 torr and temperature of 273 K is 0.081 mm [108]. This value can be extrapolated for higher temperatures (≤ 600 K) using an equation outlined by the author. So, at 1 torr and 600 K, the mean free path of argon atoms in argon is approximately 0.1 mm. STERLING and WESTWOOD [101] have reported that aluminum atoms lose about 60% of their initial energy during each elastic collision with an argon atom so that sputtered atoms with initial energies of 20 eV would possess thermal energies (approximately 0.07 eV based on a gas kinetic temperature of less than 1000 K [22]) after about 11 collisions. If one assumes that aluminum atoms possess the same mean free path as argon atoms, aluminum atoms would be diffusion controlled after having travelled 0.6 mm through the discharge. Therefore, from this simple calculation and assumptions, it appears plausible that GOUGH'S cell can reduce re-deposition.

4.3.2 The ATOMSOURCE™

Since the jets of the ATOMSOURCE™ produce a resultant flow of support gas directed away from the sample near the surface, one would assume that the extent of re-deposition reduction is equal to if not greater than that for the glass cell. The crater formation evident using the ATOMSOURCE™ is however, quite puzzling. It is most
probably due to the maximization of reduction in re-deposition where
the jets directly impinge upon the sample rather than any increase in
sputtering rate. It does not seem likely that the jets can provide any
significant additional momentum to impacting ions which would tend
to increase sputtering ratios. BOUMANS has shown that for a 700 V
GRIMM glow discharge at 10 torr of argon, the uncorrected sputtering
ratio is similar to that for a 100 eV impacting ion [18] which translates
into an ion velocity at impact of about $10^6$ cm/sec. For a 1 L/min jet
flow rate and a jet diameter of 1 mm, the velocity of argon at any one
jet tip would be about $10^4$ cm/sec which would be quickly dissipated
through collisions before impact with the cathode (ie. argon atoms
from the jet tip would experience about 20 collisions in travelling the 1
mm to the cathode surface if the mean free path is 0.05 mm). Therefore,
the velocity component attributable to the jets is
insignificant when compared to that obtained through the electric field
indicating that no measurable increase in the sputtering ratio would
result from the use of the ATOMSOURCE™ jet geometry. This supports
the hypothesis that crater formation is attributable to re-deposition
reduction.

4.3.3 Gough's Cell vs the ATOMSOURCE™

The principle difference between these two atomizers is the
introduction of the directed support gas flow: Gough's cell directs
gas parallel to the sample surface whereas the ATOMSOURCE™
directs gas at the surface. Both significantly increase atomic
populations in an analysis volume spatially removed from the sample
surface relative to a no gas flow situation as attested by absorbance
measurements; however, there appears to be a difference in how this is achieved.

GOUGH et al. have recently compared these two atomizers for analytical performance [55]. In their study, they reported that for similar pressures and discharge currents, the two sources possessed significantly different discharge voltages. They indicated that this was probably due to the fact that the pressure metering is performed some distance from the sample surface where the electrical characteristics of the discharge are set since almost all the discharge voltage is dropped in the cathode dark space. Therefore, the pressure at the metering port was quite different to that existing at the sample surface for both sources.

The ATOMSOURCE™ directs support gas at the sample surface, so one would expect that the pressure at the surface to be greater than at the metering port. This supposition is supported by KIM and PIEPMEIER [69] who showed that the voltage-current curve for a high gas-jet flow displays a shallower increase in voltage with an increase in current relative to a no gas flow situation at a similar pressure. This performance may be obtained if the pressure is greater at the sample surface for the high jet flow rate case as seen in Figure 4.2 where the voltage-current curves tend to flatten with both increasing jet flow rate and pressure. The symmetrical arrangement of the six jets produces a resultant flow of support gas near the surface, which is then directed away from the surface, thus reducing re-deposition.

Conversely, GOUGH'S cell uses a flow directed parallel to, and about 0.5 mm from, the surface. This flow of gas would effectively block any sample atom, sputtered with an ejection velocity sufficient
to carry it beyond the gas stream, from returning to the surface. However, it seems likely that only a small portion of sputtered atoms would possess sufficient energy from the sputtering process to be able to travel axially 0.5 mm before thermalization. STUART and WEHNER have shown that the sputtered atom ejection energy distribution for 600 eV Ar ion bombardment of copper has only a small high energy tail that reaches to 20 eV [103]. At 100 eV, which is a more likely average energy for incoming ions in these sources, it is expected that an even smaller proportion of ejected atoms would possess sufficient energy to travel 0.5 mm before thermalization. This would reduce the population of sputtered atoms with sufficient ejection energy to penetrate the jet stream barrier, thus allowing a greater proportion to diffuse back to the cathode.

However, the jet stream may produce other physical effects beside acting as a barrier. The high speed flow of gas directed parallel to the sample surface may produce a greater pressure at the metering port than at the sample surface. This lower pressure at the sample surface would increase the energy of incoming ions at impact due to a reduction in the collision frequency. This possibility is supported by the differences in discharge voltage (although no absolute differences were reported) for the GOUGH cell relative to the ATOMSOURCE™ [55]. The higher energy at collision with the sample surface would translate into greater sputtering ratios [74] and more energetic sputter ejections [103] allowing more sputtered atoms to travel axially further before thermalization than without a jet flow.

Further analysis of the re-deposition characteristics for the GOUGH cell is not presently possible without more data; we will now
Figure 4.2: Voltage - current curves for the jet-assisted glow discharge source at two pressures and jet flow rates: (○) - 3.7 mbar, 0 cL/min; (●) - 3.7 mbar, 30 cL/min; (□) - 9.1 mbar, 0 cL/min; (■) - 9.1 mbar, 30 cL/min.
turn our attention to the analysis of the burn spot and re-deposition processes of the jet-assisted glow discharge source.

4.4.4. Results with the Jet-assisted Glow Discharge Source

4.4.1 Cone Formation

When sputtered surfaces are analyzed under high magnification, certain features become apparent that are essentially invisible to the naked eye. Various authors have examined burn spots under high magnification using an Scanning Electron Microscope (SEM). JÄGER and BLUM have examined the burn spots from a GRIMM glow discharge, noting the existence of cones if the sample contains inclusions [66]. HARRISON et al. have reported the existence of conical structures for the argon bombardment of copper using a hollow cathode [37] and a hemispherical cathode [24] geometry. WITCOMB has discussed cone formation in stainless steel, again using argon support gas in a hollow cathode geometry [120].

These features are also apparent on the surface of a copper sample exposed to sputtering using the jet-assisted glow discharge source (Fig. 4.3a and 4.3b) with a zero gas flow rate through the jets. Using a zero gas flow rate through the jets allows the jet-assisted source to emulate a GRIMM glow discharge as an obstructed discharge ensues with support gas introduction occurring through an inlet spatially removed from the cathode surface [2]. However, if a non-zero jet flow rate is used, cones tend to localize away from the characteristic craters of the burn spots (Fig. 4.4a-4.4d). Figures 4.4a and 4.4b represent portions of the burn spot using a jet flow rate of 50
cL/min; Figs 4.4c and 4.4d. a flow rate of 90 cL/min. As evidenced from the high magnification side of the split screen, cones are present in the relatively flat portions of both burn spots removed from the craters; while the craters themselves are devoid of such features.

These findings verify those of KIM and PIEPMEIER who noted the absence of cones in the jet-induced craters of burn spots using the ATOMSOURCE™ [69]. These authors attributed this absence to erosion by the jets: they speculated that bombarding ions would possess a horizontal velocity component parallel to the sample surface which would tend to undercut cones. However, if the bombarding ions did possess a horizontal velocity component, cones would form parallel to the direction of the incident ions as found by MAGNUSON et al. [80]. This is clearly not the case as evident from Fig. 4.4 and the SEM photographs evident in KIM and PIEPMEIER'S work [69].

It is well documented that cones form due to the presence of particles resting on the surface of the sample or inclusions present in the body of the sample [99, 100, 114, 117]. This is also true of the cones evident on the burn spot of the jet-assisted glow discharge source. Figures 4.5a and 4.5b show photographs (bottom portion of the figures) with corresponding x-ray maps for silicon (upper portion of the figures) of the burn spot surface after sputtering for twenty minutes. Each bright spot on the x-ray map represents a detectable amount of silicon x-ray emission. If the x-ray maps are superimposed on the photographs, it becomes apparent that the clusters of bright spots originate from flat-topped cones indicating that sputter-resistant silicon is responsible for the formation of these cones.
Figure 4.3: SEM photographs of cone formation on a copper cathode after sputtering for 20 min. at 3.7 mbar, 0 cL/min and 35 W. Sample tilt of 75° from a plan view. Jet flow rate: a) 80X magnification; b) 1000X magnification.
Figure 4.4: Split screen SEM photographs of a portion of the burn spot: left-side, 30X magnification; right-side 5X magnification of the boxed area. Sample tilt of 75° from a plan view. Sputter duration of 20 min. at 5.7 mbar, 50 cL/min and 40 W. a) in crater; b) out of crater.
Figure 4.4 (cont): Split screen SEM photographs of a portion of the burn spot: left-side, 30X magnification; right-side 5X magnification of the boxed area. Sample tilt of 75° from a plan view. Sputter duration of 20 min. at 5.7 mbar, 90 cL/min and 40 W. c) in crater; d) out of crater.
STEWART and THOMPSON have explained the shape and symmetry of the cones on sputtered surfaces [100]. The cone apex angle is formed due to a sputtering ratio dependence on the angle $\Theta$, described between the path of the incident ion and the surface normal. The dependence is different for different atomic number atoms and is at a maximum when $60^\circ < \Theta < 80^\circ$. So with an inclusion exposed or a particle resting on or embedded in the surface, any projection would tend to expose a surface with greatest sputtering yield when bombarded with support gas ions. If we designate $\phi$ as the angle of maximum sputtering yield, then with the necessary inclusions or particles, a cone apex angle of $2\phi$ and semi-angle of $\pi/2 - \phi$ will form from the bombardment of ions with angles of incidence equal to the surface normal (see Fig. 4.6). So for elements with large $\phi$, squat flat cones will appear; elements with small $\phi$ will possess sharp cones.

A reason for cone absence in the craters now becomes apparent. In the jet-assisted glow discharge source, the sample surface is bathed in support gas, especially where the jets impinge on the surface - at the craters. One would expect the collision frequency to be greater in this particular region of the burn spot which would tend to randomize $\Theta$, the angle the incident ions make with the surface normal, giving it a larger distribution of angles. With no unique $\Theta$, it would be difficult to expose a maximum sputtering yield surface, therefore retarding cone formation.

The origin of the silicon present on the burn spot is an interesting issue in this study. It was originally thought that the silicon originated from the pump oil, but since we use DuoSeal, which is a paraffin-based oil, this is not likely. More probable is that grains of
Figure 4.5: Split screen SEM photographs of cones on the burn spot using 5.7 mbar, 50 cL/min and 40 W for 20 min. Sample tilt of 0° from a plan view. Left-side is an x-ray map of silicon: each point of light represents a quantifiable amount of Si x-rays; right-side is a pictorial representation of the same area. a) 500X mag; b) 1100X mag.
Figure 4.6: Schematic representation of a cone on the surface of a sample which has been sputtered.
silicon carbide were deposited during sample preparation using DURITE® abrasive paper to remove the oxide layer from the copper surface. Embedded silicon carbide would protect the copper surface during sputtering allowing cone formation. Furthermore, only silicon could be detected since the EDX analysis was incapable of detecting carbon. This would also explain the relatively unsymmetrical features of the silicon-topped cones since they would undoubtedly follow the shape of the silicon imbedded in the copper from the abrasion.

To verify the hypothesis that silicon-capped cones originate from the sample preparation, a copper cathode was cleaned using a hydrochloric acid bath to remove the oxide layer instead of using DURITE® abrasive paper. The surface was then washed with water and dried with methanol. After sputtering the surface for twenty minutes, individual cones formed which possessed predominantly aluminum caps (see Fig 4.7). Other features were also apparent. After sample preparation without the silicon carbide paper, the surface still had what appeared to be scratches on its surface. After sputtering, a line of cones was found (see Fig. 4.8) which may have originated from one of these scratches. The top of this line of cones was not uniform but changed significantly along its length. Table VI displays the various elemental concentrations of the cone tops for each of the SEM figures showing cones. It appears that the surface features of a sputtered sample are acutely susceptible to the method of sample preparation. The use of abrasive paper will leave particulates embedded in the sample which will act to form cones. If the frequency of cone formation is significant, one can imagine that this would be a consequence that could effect the depth profiling of
Figure 4.7: Split screen SEM photographs of a cone on the burn spot using 5.7 mbar, 0 cL/min and 40 W for 20 min.. Sample tilt of 0 ° from a plan view. Sample preparation consisted of an acid washing. Left-side is an x-ray map of aluminum: each point of light represents a quantifiable amount of Al x-rays; right-side is a pictorial representation of the same area. Magnification is 1500X.
Figure 4.8: SEM photograph of a line of cones on the burn spot using 5.7 mbar, 0 cL/min and 40 W for 20 min.. Sample tilt of 0° from a plan view. Sample preparation consisted of an acid washing. Magnification is 300X.
Table VI: Cone top elemental concentrations for various cone formations found on sputtered surfaces using the jet-assisted glow discharge source

<table>
<thead>
<tr>
<th>Figure No.</th>
<th>Cu</th>
<th>Si</th>
<th>Al</th>
<th>Na</th>
<th>Ca</th>
<th>Ti</th>
<th>Mg</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>5.2</td>
<td>94.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5b</td>
<td>3.2</td>
<td>96.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>94.6</td>
<td></td>
</tr>
<tr>
<td>8, Cone top at bottom right corner</td>
<td>8.7</td>
<td>49.0</td>
<td>25.5</td>
<td>9.3</td>
<td>4.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8, Cone top at middle of line of cones</td>
<td></td>
<td></td>
<td>57.7</td>
<td>12.4</td>
<td>15.3</td>
<td>11.4</td>
<td></td>
<td>3.2</td>
</tr>
<tr>
<td>8, Cone top at upper left corner</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>
samples if a resolution of less than the cone height (typically 20 - 50 μm) is required.

4.4.2 Re-deposition

Other physical effects on the burn spot manifest themselves under the scrutiny of the SEM. Figure 4.9a is a photograph at 200x magnification of the burn spot edge using a zero jet flow rate. The foreground of the photograph displays typical sputter etching, but the edge in the upper portion of the photograph displays features more commonly seen in thin film deposition studies. It appears that significant deposition occurs along the edge of the burn spot where no sputtering occurs. This is supported by FERREIRA and BÜGER who found significant deposition in the anode-cathode gap region using a GRIMM glow discharge [48]: this area would also experience no sputtering due to the narrow width of the gap [18]. If a jet flow rate of 10 cL/min is used (Fig. 4.9b), the beginnings of deposition under the lip of the edge deposition is apparent. At higher jet flow rates, significant deposition under the lip is seen at the edge of the burn spot removed from any of the six jets (Fig. 4.9c); but this deposition is reduced where the jet flow contacts the sample (Fig. 4.9d). Therefore, although the use of jets may impede diffusion-controlled re-deposition of sputtered species over the whole burn spot, the dynamic flow enhances, to some extent, edge deposition.

Quantification of edge deposition is possible using the sample holder described in Section 4.2.3. The experiment was performed using copper and brass samples held together to form a single cathode. Figure 4.10 is a photograph of the copper (< 0.01 % zinc)
Figure 4.9: SEM photographs of the edge of the burn spot using 5.7 mbar and 40 W for 20 min. Sample tilt of 75° from a plan view. Magnification is 200X. a) 0 cL/min; b) 10 cL/min.
Figure 4.9 (cont): SEM photographs of the edge of the burn spot using 30 cL/min, 5.7 mbar and 40 W for 20 min. Sample tilt of 75° from a plan view. Magnification is 200X. c) out of crater; d) in crater.
half of the cathode, after sputtering with a 50 cL/min jet flow rate, showing the edge of the burn spot used in the re-deposition analysis (running along the diagonal upper left-hand corner to lower right-hand corner). The burn spot itself is located in the upper right-hand third of the photograph. The edge of the burn spot in the extreme lower right-hand corner was in the closest proximity to the brass half of the cathode. Using Energy Dispersive X-ray Fluorescence, this area of the edge, approximately 0.05 mm from the brass (29.0 % zinc), had a surface zinc content of 24.1 %. Deposition attributable to the brass diminishes rapidly with distance from the brass half of the cathode (Fig. 4.11): at 1 mm from the brass, there is less than 0.5 % zinc redeposited at the edge indicating that edge deposition is extremely localized.

The evaluation of re-deposition on the burn spot itself is more difficult since atoms deposited are re-sputtered. Furthermore, they are more likely to be re-sputtered than atoms contained in the matrix since their association with the surface is less tenacious. In redepositing, they are essentially condensed out of the gas phase onto the water-cooled cathode.

FERREIRA and BÜGER have estimated that 17 % of atoms sputtered using a GRIMM glow discharge are redeposited on the burn spot [48]. This experiment used a copper rod, 1 mm in diameter, inserted into the center of an aluminum disc which was then sputtered under typical analytical conditions (1200 V, 50 or 100 mA). The percentage re-deposition was evaluated from the ratio of redeposited copper on the aluminum disc to copper atoms sputtered from the insert obtained using an ion microprobe mass analyzer (IMMA). It
Figure 4.10: SEM photograph of a copper cathode burn spot edge using 5.7 mbar, 50 cL/min and 40 W for 20 min. The brass cathode was in contact with the copper cathode in the bottom right-hand corner of the photograph. The burn spot is visible in the top right third of the photograph; the remaining two thirds shows unsputtered cathode. Sample tilt of 0° from a plan view. Magnification is 300X.
Figure 4.11: Zinc re-deposition on the copper cathode at the edge of the burn spot. Percentage of zinc variation with distance from the brass cathode. Discharge conditions: 5.7 mbar, 50 cL/min and 40 W.
appears that the authors did not account for re-deposition onto the copper insert itself which should be significant due to the localized nature of the process: FERREIRA and BÜGER themselves demonstrate that the IMMA counts attributable to copper deposition drop by almost an order of magnitude 1 mm from the copper insert. Therefore, it is very likely that the value of 17 % underestimates re-deposition in the GRIMM glow discharge.

KIM and PIEPMEIER [69] have performed a similar experiment to that of FERREIRA and BÜGER using the ATOMSOURCE™, although their results were more qualitative. They inserted a non-conducting lava rod of approximately half the diameter of the burn spot, into a brass cathode then sputtered the sample with a high jet flow rate. They found traces of brass on the lava rod along the edges of the jets indicating that re-deposition was occurring in the burn spot.

The absolute quantification of re-deposition in analytical glow discharges is fraught with assumptions and approximations which brings into question the result obtained. A more useful approach may be to evaluate the relative performance between sources. The reduced sputtering rate is defined as the weight loss from the sample per unit time normalized for discharge current changes [18]. If a constant voltage is maintained along with a similar current, the reduced sputtering rate can be used to indicate differences in re-deposition for different sources assuming similar sputtering rates.

From Table VII, it is apparent that the reduced sputtering rate is essentially the same for a planar diode geometry, the GRIMM source and the jet-assisted source operated with a zero flow rate through the jets indicating that similar sputtering/re-deposition processes are
occurring. However, with a 90 cL/min jet flow rate, the reduced sputtering rate is more than a factor of three greater than the other values for static discharges. As earlier indicated, there is little likelihood that the jet flow rate would produce any increase in sputtering ratio, therefore one can assume that the bulk of the increased reduced sputtering rate apparent for the 90 cL/min flow rate case is directly attributable to a reduction in re-deposition on the sample surface.

Figure 4.12 displays sample loss rate increases with jet flow rate at a constant voltage and current. Keeping these parameters constant should yield a similar pressure in the cathode dark space for each of the jet flow rate settings ensuring that bombarding ion populations and collision frequencies in the dark space are comparable. From the figure it is apparent that re-deposition reduction is not a linear process with increasing jet flow rate: very low flow rates appear to reduce re-deposition marginally until flow rates of greater than 10 cL/min are used. Also, after 50 cL/min, the increase in re-deposition reduction begins to tail-off.

This shape is quite dissimilar to that obtained in a previous study [2]: the previous Figure of sample loss rate versus jet flow rate displayed a sample loss rate insensitivity to jet flow rate increases at relatively low jet flow rates. At 20 cL/min, the sample loss rate appeared to near a plateau where greater jet flow rates would have little effect on increasing the sample loss rate. That is clearly not the case in Figure 4.12, where sample loss rates are still increasing at 90 cL/min. The reason for this discrepancy is due to the localized increase in pressure at the sample surface caused by the jets. The
Table VII: Comparison of the reduced sputtering rate of different glow discharge sources in argon at a discharge voltage of 600 V

<table>
<thead>
<tr>
<th>SOURCE TYPE</th>
<th>PRESSURE (mbar)</th>
<th>CURRENT (mA)</th>
<th>JET FLOW RATE (cL/min)</th>
<th>REDUCED SPUTTERING RATE (µg/A sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>planar diode [58]</td>
<td>6.7</td>
<td>39</td>
<td>-</td>
<td>230</td>
</tr>
<tr>
<td>GRIMM [1]</td>
<td>13.3</td>
<td>108</td>
<td>-</td>
<td>200</td>
</tr>
<tr>
<td>jet-assisted</td>
<td>4.7</td>
<td>40</td>
<td>0</td>
<td>220</td>
</tr>
<tr>
<td>jet-assisted</td>
<td>6.0</td>
<td>100</td>
<td>90</td>
<td>700</td>
</tr>
<tr>
<td>jet-assisted</td>
<td>7.6</td>
<td>101</td>
<td>0</td>
<td>230</td>
</tr>
</tbody>
</table>
Figure 4.12: Sample loss rate vs. jet flow rate at a constant voltage and current (600 V, 100 mA).
previous experiment to determine jet flow rate effect on sample loss rates was done at a constant pressure; however, both voltage and current dissipated in the discharge could not be kept constant. The higher flow rates typically possessed lower voltages and higher currents than their lower flow rate counterparts indicative of the localized increase in pressure at the sample surface which is spatially removed from the pressure metering port on the source body (see Fig. 4.2).

Although higher currents indicate higher bombarding ion populations, lower voltages provide bombarding ions with less energy, reducing the sputtering ratio. Furthermore, the higher pressure would increase the collisional frequency of the bombarding ions, lowering the energy available at collision with the sample surface and therefore exacerbating the reduction in sputtering ratio. For these reasons, one would expect that in the previous, constant pressure, study, lower jet flow rates would possess a larger sputtering ratio than higher flow rates. For Figure 4.12, the pressure in the port is not kept constant, but the voltage and current are. The reduction in metered pressure required to maintain constant voltage and current conditions as the jet flow rate is increased is show in Fig. 4.13. These conditions should maintain a constant sputtering ratio with changing jet flow rate allowing the direct assessment of re-deposition reduction from sample loss rate data.

4.5. Summary

The use of jets to direct support gas at the cathode produces inhomogeneous conditions at the sample surface. Significant
Figure 4.13: Pressure required to maintain constant voltage, constant current conditions as the jet flow rate is changed.
cratering on the sample reflecting the hexagonal symmetry of the jet geometry attests to this conclusion. In the craters, the formation of protruding surface features originating from the sputtering process is impeded due to a greater distribution of bombarding ion incidence angles preventing a maximum sputtering yield surface from being established. This greater distribution is created by higher collisional frequencies with support gas atoms, specifically at the jet-sample impingement locations.

Similarly to static gas flow glow discharges like the GRIMM source, substantial sputtered atom re-deposition is found at the edges of the burn spot for the jet-assisted glow discharge source. Unlike static gas flow glow discharges, however, a substantial reduction in re-deposition is evident using support gas jets as determined by weight loss measurements. The reduction is principally localized where the support gas flow impinges on the sample surface producing the characteristic craters. Therefore, the sampling efficiency for the jet-assisted glow discharge is a factor of three greater than that for static gas flow discharges.
CHAPTER 5

ATOMIC EXCITATION IN A JET-ASSISTED GLOW DISCHARGE
PLASMA PLUME

5.1 Introduction

The jet-assisted glow discharge source, constructed in-house and modelled partially on the ATOMSOURCE™ and on the GRIMM glow discharge source, was shown to suffer from the self-absorption of atomic resonance emission lines and other lines of appreciable absorption coefficient in Chapter 3 and in a past publication [3].

In characterizing the self-absorption problem present in the jet-assisted source, two side optical ports were added to the original source body allowing both absorbance and emission measurements to be obtained of the jet-assisted plasma plume and regions beyond its extension at an appreciable distance from the cathode surface. Emission intensities of the Fe I resonance line at 371.99 nm was shown to increase with increasing jet flow rate when viewed through the side optical ports in contrast to the response when viewed through the original end optical port, although the magnitude of the intensity was appreciably smaller.

Viewing the jet-assisted plume laterally, with a viewing axis that bisects the plume, substantially reduces the absorption path length relative to viewing end-on (axially) with the viewing axis running the full length of the plume. Therefore, one would expect that self-absorption would be significantly reduced, if not eliminated, by viewing laterally. However, in viewing laterally, the plume that
extends beyond the tubular anode housing is sampled. It is extremely
doubtful that the electric field generated by the potential difference
between the cathode and anode extends beyond the anode. Therefore one would expect that the plume that extends beyond the
anode no longer has any dc power coupled into it, but rather decays
with increasing distance from the electric field that generated the
energetic particles that sustains the discharge.

In this Chapter, our aim is to investigate the excitation of
sputtered species in the plasma plume of the jet-assisted glow
discharge source.

5.2. Experimental

5.2.1 The Jet-assisted Glow Discharge Source

The jet-assisted glow discharge source has been described in
previous Chapters and publications [2-4], although several
modifications were made to allow the jet-assisted plume to be viewed
as close to the sample surface as possible. To do this, the Delrin\textsuperscript{TM} flange [2] was replaced by a brass flange with a 90\degree bend and a
Delrin\textsuperscript{TM} top to form the necessary electrical insulation between the
sample and source body (Fig.5.1). With the brass/Delrin\textsuperscript{TM} flange in
place, the plume could be viewed at an axial distance of 25 mm from
the sample surface. In addition, an aluminum insert was placed in the
hollow anode to form a hollow cylinder which was better able to
collimate the plume as it issued from the anode housing into the
analysis volume.
Figure 5.1: Schematic diagram showing a cross-section of the jet-assisted glow discharge source using the brass/Delrin™ flange to allow viewing of the jet-assisted plasma plume at a closest axial distance of 25 mm from the sample surface.
2.2 Radially-resolved Spatial Emission Intensity Maps

The spatial emission characteristics of the jet-assisted plume were obtained using a SCHOEFFEL-MCPHERSON 1-m CZERNY-TURNER monochromator described previously in Chapter 3. Light detection was performed using a Reticon (Sunnyvale, CA) Model RL-4096S linear photodiode array (LPDA) which consisted of 4096 discrete photodiodes 7 μm wide on 15 μm centers. The height of each photodiode was 0.5 mm and the overall length of the light sensitive area was 61.44 mm. This LPDA was also cooled and its readout obtained in a similar fashion to that described previously in Chapter 3.

In order to obtain spatial emission characteristics of the plume, the LPDA was orientated axially to the plume so that the length of the LPDA provided a vertical profile of the jet-assisted plume. Vertical slices of the plume along its complete width with a lateral resolution of 0.127 mm were obtained by scanning across the plume in 120 steps to a total distance of 15.24 mm. The entire source was mounted on a Daedal (Harrison, PA) stepper motor driven linear translation stage which was controlled by the Telex computer described in Chapter 3.

Radial resolution was then provided by performing an ABEL inversion on the lateral scans. This is a mathematical operation which successively subtracts emission from outer layers of the plasma allowing the emission from inner layers to be independently quantified. A simple analogy which describes the ABEL inversion process is peeling layers of an onion. The outermost layer is quantified first; then a second layer is examined, the emission attributable to the first layer is subtracted from the total emission of
the layer which leaves emission attributable to the second layer. This process is continued across the plasma. With a lateral scan totalling 120 steps, it was possible to independently quantify 60 plasma layers. For a more complete description of ABEL inversion, the reader is directed to reference [28].

An axial resolution of 0.30 mm was obtained by batching groups of 20 diodes together and averaging their output. A reciprocal linear dispersion of 0.655 nm/mm was calculated for the Cu I 515.32 nm emission line according to the procedure outlined by WÜNSCH et al. [121] which produces a wavelength window of 0.328 nm for the width (0.5 mm) of the vertically-orientated LPDA. Emission lines chosen for the investigation of their spatial emission characteristics in the plume had to demonstrate a freedom from spectral interferences over this complete wavelength window.

5.2.3 Spectra and Optical Measurements using Photomultiplier Detection

Other optical measurements were obtained using a SCHOEFFEL-MCPHERSON 0.35-m CZERNY-TURNER monochromator and detection system previously described [2]. Output from the current amplifier was coupled into a Stanford Research Systems (Palo Alto, CA), Model SR245 computer interface module where the analog signal was converted into digital form at a rate of 10 Hz. This allowed a computer to collect spectra which could be corrected for the spectral response of the dispersion and detection system. This was accomplished using an Electro Optics Associates (Palo Alto, CA)
Model L-10 quartz-iodine tungsten filament standard lamp supplied with an Electro Optics Associates Model P-101 power source [96].

Absorbance measurements were obtained using hollow cathode lamps (HCL) powered by a pulsed power supply constructed in Electronics, Department of Chemistry, UBC. The power supply was capable of delivering up to 100 mA of current at modulation frequencies of up to 500 Hz. The modulated radiation from the HCLs was differentiated from the plume emission using a Princeton Applied Research (Princeton, NJ) Model 120 lock-in amplifier/phase detector. Argon metastable absorbance measurements were obtained using a Mercury HCL which was filled with argon.

5.3. Results and Discussion

5.3.1 Spatial Emission Characteristics of the Jet-induced Plasma Plume

Figure 5.2 is a schematic representation of the jet-assisted plume as it extends beyond the hollow cylindrical anode under the influence of a relatively large jet flow rate. The schematic is a realistic representation with regard to the shape of the plume: little or no visible emission is apparent beyond a cylinder subtended by the inner dimensions of the aluminum insert which is roughly 10 mm in diameter. Figure 5.3 is the radially-resolved surface (left-side) and contour (right-side) maps depicting the distribution of Cu I 515.32 nm emission in the jet-assisted plasma plume at a jet flow rate of 50 cL/min. It is evident that the plume is confined in the radial direction to the inner dimensions of the aluminum insert. Also, the emission
Figure 5.2: Schematic diagram illustrating how the jet-assisted plume issues from the anode housing.
Figure 5.3: Radially-resolved spatial emission intensity surface map for Cu I 515.32 nm at a jet-flow rate of 50 cL/min, power of 40 W and metered pressure of 3.7 mbar. Inset is a topographical representation of the surface.
intensity drops rapidly as the radial distance from the plasma plume center is increased, especially close to the aluminum insert. However, it extends considerably further axially following the support gas flow generated by the jets. This axial jet flow becomes obvious as the support gas flow through the jets is manipulated. Figure 5.4 contains radially-resolved surface maps depicting the same Cu I emission at 515.32 nm for different flow rates and pressures all drawn to the same scale using the same axes as Fig. 5.3. The surface in Fig. 5.4b was obtained using a jet flow rate of 30 cL/min at a pressure of 3.7 mbar. The magnitude of the emission is considerably less than that apparent for the 50 cL/min flow rate case shown in Fig. 5.4a over the whole surface. In addition, the emission at 30 cL/min extends axially out of the anode only marginally. The axial extension of the plume at low flow rates is reduced further if the pressure is increased as in Fig. 5.4c. However, if the jet flow rate is substantially increased, as in Fig. 5.4d to 90 cL/min, the plume extends the full length of the viewing window, although the magnitude of the emission is attenuated with axial distance from the cathode. It is interesting to note that the magnitude of emission at 25 mm from the cathode surface is greater for a 50 cL/min flow rate relative to a 90 cL/min flow rate, although more emission is seen at axial distances greater than 35 mm for the higher flow rate. The amount of material sputtered is similar for both flow rates at similar metered pressures [5], therefore this indicates that the higher flow rate tends to radially spread the sputtered material more than the lower flow rate.
Radially-resolved spatial emission intensity surface maps for Cu I 515.32 nm at various conditions (power: 40 W). a) discharge conditions identical to Fig. 3; b) 30 cL/min, 2.9 mbar; c) 30 cL/min, 5.7 mbar; d) 90 cL/min, 5.7 mbar. Surface base (axial and radial position) used is identical to Fig. 3. All plots have the same emission intensity scale factor.
From the radially-resolved surface emission intensity maps of the Cu I line, it is apparent that emission intensity steadily decays as the axial distance from the cathode is increased. If the natural logarithm of the emission intensity decay from the plume center is plotted against axial distance from the cathode, a straight line should result if the decay in emission is exponential.

Figure 5.5 is the natural logarithm of the radially-resolved axial profile of three emission lines from the center of the plasma plume as it extends out of the anode. It appears that the same exponential decay for the Cu I 515.32 nm line also fits the Ar I line at 696.54 nm reasonably well. The greater dip in the experimental markers seen for the Ar I line at higher axial distances is a result of greater radial diffusion: argon atoms are less massive than copper atoms and will therefore possess a greater diffusion coefficient resulting in more radial diffusion out of the analysis volume. However, using data from Table VI, these two emission lines possess natural radiative lifetimes that differ by an order of magnitude (Cu - 1.7x10^{-8} sec, Ar - 1.5x10^{-7} sec). Therefore, one would expect dissimilar exponential decays if the curves represent excited state decay. Figure 5.5 also contains the results for Cu I 406.32 nm. This emission line possesses a longer natural radiative lifetime (4.8x10^{-8} sec) and a more energetic excited state relative to the “green” line (6.87 cf. 6.19 eV). From the figure, it is apparent that both behave equally which supports the evidence from the Cu/Ar comparison.

Since it is clear that the decay in the emission signal is not due to the natural radiative lifetimes of the specific transitions investigated, it is probable that the response is attributable to the
Figure 5.5: Natural logarithm of radially-resolved emission intensity axial profiles from the center of the jet-assisted plume: (○) - Cu I 515.32 nm; (●) - Cu I 406.26 nm; (△) - Ar I 696.54 nm. Discharge conditions identical to those described in Fig. 5.3.
decay of the exciting medium or media. In glow discharges, negative glow excitation is dominated by electron impact at pressures typically used for analytical purposes [22]. However, in the case of the jet-induced plume, one may ask the question: "is it the negative glow that extends beyond the anode housing or is it some form of flowing afterglow?"

5.3.2 Fundamental Considerations

In a glow discharge, secondary electrons, produced through plasma particle collisions with the cathode, are accelerated from the cathode by the electric field and travel across the cathode dark space to the negative glow. At this point the electric field has been reduced to a very small fraction of the original value and the kinetic energy of the electrons is consumed by collisions with sputtered and support gas atoms [63]. This results in their excitation and resulting spontaneous emission producing the luminous negative glow region. DOGAN et al. have shown that for a GRIMM lamp, the radiating layer, which is essentially the negative glow, is very thin [39]: it typically stretches less than 2 mm axially when monitoring the Fe I resonance line at 371.99 nm at 25 Watts and 13.3 mbar. This thickness doubles when the discharge power is increased to 80 Watts. Other emission lines demonstrated similar behavior. Since the boundary between the cathode dark space and the luminous region marks the "extinguishing" of the electric field, it appears that the electric field is relatively localized near the sample surface in a GRIMM glow discharge.
The jet-assisted glow discharge source is essentially a GRIMM lamp with support gas jets included. Although side-viewing near the cathode surface is impossible with the present experimental apparatus, the luminous portion of the glow discharge viewed axially appears restricted to an area in close proximity to the cathode, when no support gas is issued through the jets, emulating DOGAN'S findings. However, when a jet flow rate of greater than 20 cL/min is used and pressures of about 3-5 mbar, the plasma plume is seen to extend beyond the anode: an axial distance of more than 25 mm from the cathode. This represents an order of magnitude increase in the length of the luminous region of the discharge (if it is in fact continuous).

As earlier indicated, the dominant excitation process occurring in the negative glow is electron excitation. Therefore, to extend the negative glow, the jet flow rate should be able to transport electrons to the visible plume. This conjecture can be assessed by two simple calculations. The velocity of gas as it travels up the anode housing can be approximated knowing the flow rate of gas as it enters the jets, the source pressure, the discharge temperature and the cross-sectional area of the six jets and the internal diameter of the anode housing. The gas flow rate in the source before it enters the jets can be calculated by the following equation [49]:

\[ V_v = V_a \frac{P_a T_v}{P_v} \]  

(5.1)
, where subscript "v" refers to vacuum, subscript "a" to atmosphere. For a gas flow rate of 50 cL/min, a pressure of 5 mbar, and an assumed temperature of 900 K obtained from the literature [50], a flow rate of 5500 cm/sec was calculated. Then, considering the cross-sectional area of the six jets and its ratio to the internal diameter of the anode housing (about 1:10), a value for the carrier gas velocity up the anode housing was calculated to be approximately 100 m/sec.

Conversely, the speed of electrons in the discharge can be calculated assuming a MAXWELL distribution of speeds by [1]:

\[
F(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp \left\{ -\frac{mv^2}{2kT} \right\} \tag{5.2}
\]

and the mean speed, \( c \), is calculable from the integral:

\[
c = \int_{0}^{\infty} vF(v)dv = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_{0}^{\infty} v^3 \exp \left\{ -\frac{mv^2}{2kT} \right\}dv \tag{5.3}
\]

Assuming the distribution is GAUSSIAN,

\[
c = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{1}{2} \left(\frac{2kT}{m}\right) = \sqrt{\frac{8kT}{\pi m}} \tag{5.4}
\]

FANG and MARCUS have reported thermal electron temperatures of about 0.3 eV in a planar diode geometry glow discharge measured using a LANGMUIR probe [44]. This yields an
average electron speed of about \(3.5 \times 10^5 \text{ m/sec}\). It appears extremely dubious that the jet-induced flow of support gas can impart any directional flow to the random motion of the electrons whose velocity is more than three orders of magnitude greater: one would expect any excitation attributable to electron impact to be localized near the cathode.

This argument assumes that the negative glow begins at the same axial distance from the cathode surface when using different jet flow rates. The beginning of the negative glow is dependent on where the electric field becomes insignificant allowing electrons to decelerate through collisions. The electric field itself is generated by the formation of space charges in the discharge: the relatively heavy positively-charged support gas ions accumulate near the cathode surface primarily in the dark space; electrons accumulate in the negative glow where their velocities attained during acceleration in the field are thermalized by collisions. Since the force exerted by the electric field is attenuated with distance from the cathode and approaches zero at the boundary between the cathode dark space and negative glow, it is possible that some support gas ions created in the relatively field-free negative glow by primary electron impact could be prevented from being accelerated to the cathode by the jet flow and transported axially towards the plume. A calculation for the mean speed of these argon ions created in the glow, similar to that done for electrons, can be simply done. The more massive support gas ion would only have a mean speed of about 700 m/sec, therefore it seems plausible that the jet flow can transport ions away from the cathode.
Since large jet flow rates would tend to smear the positive space charge in the axial direction, one would surmise that an increase in the axial spread of the positive space charge would lengthen the cathode dark space. A longer dark space would result in a smaller electric field gradient resulting in a reduction of the impacting energy for cathode bombarding ions since a greater number of collisions would occur during acceleration across the dark space. A reduction in the impacting energy of support gas ions would reduce the sputtering ratio leading to a reduction in sputtering rates. In a previous paper [6], however, we found that sample loss rates increased with increasing jet flow rate which we attributed to a reduction in sputtered atom re-deposition. It may be that the extent of re-deposition reduction is greater than originally thought due to the concomitant reduction in sputtering ratio with large jet flow rates.

A longer dark space would also allow electrons to travel further axially. But it still seems unlikely that a significant proportion of electrons from the negative glow can travel the full 20-25 mm length (depending on where the cathode dark space ends and negative glow begins) of the positively-charged anode housing without recombination on its walls. JAKUBOWSKI, STEUWER and TOELG have used a GRIMM-type glow discharge operating at 5 mbar as an ion source for a quadrupole mass spectrometer [67]. The electron population of the discharge was measured using a LANGMUIR probe at two axial distances from the cathode surface: 7 and 13 mm. It was apparent that the electron density was reduced by a factor of more than 300 and the average electron temperature was reduced from 8000 to 6800 K by positioning the probe at the greater axial distance.
This indicates that the ionizing plasma present in the negative glow is being replaced by a recombining plasma at an axial distance of 13 mm: at 25 mm the discharge should more closely resemble a purely recombining plasma.

5.3.3 A Flowing Afterglow?

PRINCE, COLLINS and ROBERTSON have used a dc hollow cathode source to produce argon metastable species for the selective excitation of electronic spectra of various molecular gases [92]. The source uses a high flow of argon support gas (the argon flow velocity was reported to be 300 m/sec), similar to that used in the jet-assisted glow discharge source, to transport metastable argon atoms to a reaction chamber where the argon is admixed with the molecular gas. The authors reported a bright "conical diffusion flame," or plume, that extended some distance from the discharge chamber into the reaction chamber, although the intensity and color of the plume was strongly dependent on the discharge current. This observation was explained by the current-dependent domination of certain exciting media: electrons and argon metastable atoms. At low discharge currents, the energy of the discharge effectively populated the metastable states of argon which were then transported to the reaction chamber producing the plume. Conversely, at discharge currents greater than 10 mA, the population of argon metastable states began to diminish through excitation to radiating states by collision with energetic electrons which was reflected in a decrease in plume intensity. At currents greater than 20 mA, a steady increase in plume intensity was attributed primarily to reactions with ions and
energetic electrons and partially to metastables produced through ion-electron recombination.

The jet-assisted glow discharge source retains many of the features of the GRIMM source, notably its hollow cylindrical anode. Therefore, as previously indicated, the possibility that energetic electrons are responsible for the jet-induced plume excitation seems remote. However, argon metastable atoms would not experience any force from the electric field and are sufficiently massive enough to possess a relatively slow thermal speed allowing the jet flow rate to have an impact on their motion. Furthermore, there would be less destruction of metastable states through electron impact to higher radiating states as found by PRINCE et al. due to electron capture on the walls of the anode. This would result in a higher metastable population. In addition, metastable states are sufficiently long-lived to survive the journey from negative glow to plume. According to FUTCH and GRANT [52], the mean life of the $^3\text{P}_2$ metastable level is about 1 msec at 5 mbar. So, using a 50 cL/min jet flow rate, where the carrier gas velocity was calculated to be 100 m/sec, a metastable atom could be transported about 10 cm before it is removed from the metastable state. Conversely, an atom in a radiating state, such as that involved in the Ar I 415.86 nm transition with a lifetime of 0.69 μsec, would only travel axially 0.0069 cm before decaying to its lower energy level.

Argon metastables are typically thought to be responsible for PENNING ionization of sputtered species [59] rather than their atomic excitation since the potential energy available (11.54 and 11.72 eV) far exceeds the first ionization limit of all metals. To conserve energy, the excitation of the Cu I 515.32 nm line by an argon metastable atom
will require the excess energy (about 5 eV) to be dissipated as kinetic energy in the recoiling atoms: not a probable event. It is possible that recombination radiative decay occurs, however. In this scheme, the PENNING ionized atoms occupy an excited ionic state which decays to the ground state of the ion. Atomic transitions are possible after the ion recombines with electrons. However, for this to occur, ionic excited states must exist and evidence of ionic radiative relaxation should be evident in spectra. This is not the case in the jet-assisted glow discharge plume.

STRAUSS, FERREIRA and HUMAN have reported argon ionization through the collision of two argon metastable species [102]. The authors were investigating persistent sputtered atom emission during the afterglow of a pulsed glow discharge. They proposed the formation of metastables in the afterglow by three body recombination of Ar ions to an atomic energy state close to the ionization limit: a RYDBERG state. This is followed by electron cascade to the 5p states which radiatively decay to either of the metastable states, $^3P_0$ and $^3P_2$:

\[
\begin{align*}
(Ar^+ + e^-) + e^- & \rightarrow Ar_R^* + e^- \\
Ar_R^* + e^- & \rightarrow Ar_{5p}^* + e^- \\
Ar_{5p}^* & \rightarrow Ar_{4s}^m + h\nu_{Ar}
\end{align*}
\]  
(5.5)
This process is fed during the afterglow by collisions between two metastable species which produces a ground state argon ion and atom and an electron:

\[ \text{Ar}^m + \text{Ar}^m \rightarrow \text{Ar} + \text{Ar}^+ + e^{-}_{\text{fast}} \]  

(5.6)

This latter reaction has been shown to possess a very high total ionization cross-section [122], therefore, despite a relatively small population of argon metastable species, some believe that reaction (5.6) is a major source of argon ions in analytical plasmas [107]. The energy difference between the sum of excitation potentials of the two metastable species and the ionization limit of the atom, which is between 7.32 and 7.68 eV depending on which states are involved, is accounted for in the kinetic energy of the resulting electron. STRAUSS et al. claim that these electrons are responsible for the continued sputtered atom excitation in the afterglow:

\[ \text{M} + e^{-}_{\text{fast}} \rightarrow \text{M}^* + e^{-}_{\text{slow}} \]

\[ \text{M}^* \rightarrow \text{M} + h\nu_{\text{M}} \]  

(5.7)

The slow electron has a greater recombination cross-section than the fast electron produced by the collision of metastables and is therefore capable of sustaining the initial recombination reaction.

The production of ions through metastable collisions in pulsed afterglows has been described and evaluated by BIONDI [15, 16] and by PHELPS and MOLNAR [89] for noble gases. Their work forms the basis for the arguments of STRAUSS et al. concerning the continued
copper emission in their pulsed afterglow. However, various studies have shown that there is significant 2-body recombination that has not been attributed to radiative (5.8), but to dissociative processes (5.9) which are characterized by large cross-sections [7, 8, 35]:

\[
\begin{align*}
\text{Ar}^+ + e^- &\rightarrow \text{Ar}^* + h\nu \quad (5.8) \\
\text{Ar}_2^+ + e^- &\rightarrow (\text{Ar}_2^*)_{\text{unstable}} \rightarrow \text{Ar}^* + \text{Ar} + \text{K.E.} \quad (5.9)
\end{align*}
\]

This excited state of argon, \( \text{Ar}^* \), is analogous to the \( \text{Ar}_R^* \) state of the three body recombination of argon outlined in (5.5), therefore the production of metastable argon excited states and the resulting argon recombination radiation should still be apparent. The argon dimer ion can be produced either by a two step process involving a) electron impact to produce an argon atom occupying a RYDBERG state; followed by b) collision between the excited atom and a ground state argon atom to provide the dimer ion [62]:

\[
\begin{align*}
\text{Ar} + e^- &\rightarrow \text{Ar}_R^* + e^- \\
\text{Ar}_R^* + \text{Ar} &\rightarrow \text{Ar}_2^+ + e^-
\end{align*}
\quad (5.10)
\]

or by a three body reaction involving an argon ion and two ground state argon atoms [17]:

\[
\text{Ar}^+ + \text{Ar} + \text{Ar} \rightarrow \text{Ar}_2^+ + \text{Ar} \quad (5.11)
\]

It is unlikely that sufficiently energetic electrons are present in the jet-induced plume to excite argon to a RYDBERG state of approximately 15 eV [62], so the three body reaction appears more plausible.
Furthermore, it has been shown that at 10 torr (13.3 mbar), noble gases are readily converted to the dimer ion by reaction (5.11) [90]. However, even with dissociative recombination, the end result is the same: the plume emits sputtered atom and argon recombination radiation.

The existence of the argon dimer ion in analytical plasmas has been verified by various authors using mass spectrometry. JAKUBOWSKI et al. [67], using a GRIMM-type glow discharge operating at 5 mbar as an ion source for a quadrupole mass spectrometer, have sampled the discharge at two axial positions relative to the cathode surface. Bulk plasma sampling was obtained by measuring the DEBYE length using an electrostatic probe and ensuring that it was sufficiently smaller than the source exit orifice diameter. At an axial distance of 7 mm from the cathode surface, a significant Ar$_2^+$ peak was apparent in the mass spectrum. The relative intensity of this peak was increased compared to the Ar$^+$ peak to the point where their intensities were approximately equal (if the hydrides ArH$^+$ and Ar$_2$H$^+$ are included) when the axial distance was increased to 13 mm. This suggests that either reaction (5.11) was progressing at a greater rate or the extent of argon ionization through electron impact or other negative glow ionization processes was reduced. PIEPMEIER et al. have used a jet-enhanced sputtering cell, similar in design to the jet-assisted source used in this report, as an ion source for mass spectrometry [70]. Their results also indicate a significant amount of the argon dimer ion relative to the argon ion at a source pressure of 2
Figure 5.6: The metastable collision cycle which requires the input of metastable atoms from the negative glow to produce energetic electrons capable of producing atomic excitation for states below approximately 7.9 eV.
torr (2.7 mbar), jet flow rate of 0.2 L/min and an axial distance of 10 mm from the cathode.

The possibility that argon atoms residing in metastable energy levels are responsible for the bulk of the excitation in the jet-induced plume now appears plausible. Metastables are not only produced in the negative glow and transported to the plume but they are also produced by the dissociative recombination of the argon dimer ion and also, to a lesser extent in analytical glow discharges, by radiative recombination involving both one and two electrons. The collision of two metastables, which is favoured through a high collisional cross-section, produces an argon ion, which can then be used to produce more argon metastable atoms, and an energetic electron that can excite most atomic states of sputtered metals. This cyclic process, the metastable collision cycle, is shown in Figure 5.6.

To this point, no empirical evidence has been offered for the metastable collision cycle in the jet-assisted plume. Verification may be obtained by looking for the by-products of the process: a) fast electrons with an energy range between 7.32 and 7.68 eV which can be indirectly accessed by examining the excitation of atomic energy states in sputtered atoms and b) argon atom radiation attributable to spontaneous emission from the 5p to 4s state (equation 5.5).

5.3.4 Spectra and State Distributions of Copper and Zinc

Figure 5.7 is a copper (99.9%) spectrum from 300 to 600 nm using a jet flow rate of 50 cL/min which has been corrected for the spectral response of the monochromator. The spectrum is dominated by copper atom lines with the exception of the two Cu II
Figure 5.7: Copper spectrum from 300 to 600 nm which has been corrected for the spectral response of the monochromator and PMT used. Emission lines designated with an asterisk are listed in Table VIII and used in Fig. 5.8. Discharge conditions are similar to those used in Fig. 5.3 with the exception of power: 25 W.
lines (appearing as second order emission lines) which are attributed to a charge transfer reaction between an argon metastable state in close proximity to the ion ground state [98]. Argon atom emission at 415.86 and 420.08 nm, which is due to spontaneous emission from the 5p to 4s state, is present but quite weak relative to the sputtered atom emission. Of more consequence, however, is the absence of any Ar II emission which is so prevalent in the negative glow of conventional glow discharges; and yet, significant emission from Cu II 224.70 nm (Second order: 449.40 nm) is apparent. This indicates that the Ar ion is present in the plume in significant quantities, but it can not be excited to any of its radiative energy states which are about 20 eV above the ground state of the ion. This finding lends credence to the idea that the plume is essentially a recombining plasma with little similarity to a negative glow and supports the metastable collision cycle shown in Figure 5.6.

Relative populations of the energy states for those transitions labelled with an asterisk in Figure 5.7 are shown in Figure 5.8. All relevant spectroscopic data for each transition are listed in Table VIII. The two vertical lines in Figure 5.8 at energies of 7.3 and 7.7 eV correspond to the minimum and maximum energy limits for electrons produced in the collision of two argon metastable atoms. It is apparent that the states in closest proximity to this energy range are significantly over-populated relative to states of lesser energy. The first ionization limit of copper is only 0.05 eV beyond the maximum electron energy limit although autoionizing radiative energy states exist above this limit at 7.74 eV and higher. No emission from these states was detected in the jet-assisted plume; whereas in the
Figure 5.8: State distributions for copper obtained using emission intensities from Fig. 5.7. Minimum and maximum e⁻ Limits refers to the minimum and maximum energy associated with the electron produced from the collision of two argon atoms in metastable states. The energy limits assume that all excess energy produced by the collision of metastable argon atoms is converted into the kinetic energy of the resultant electron.
Table VIII: Spectroscopic data for the transitions labelled in Figs 5.8 and 5.10 [93] except where asterisked [67]

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
<th>Energy (eV)</th>
<th>gA (10^8 sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>306.34</td>
<td>5.69</td>
<td>0.062</td>
</tr>
<tr>
<td>Cu*</td>
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<td>0.070</td>
</tr>
<tr>
<td>Cu</td>
<td>319.41</td>
<td>5.52</td>
<td>0.062</td>
</tr>
<tr>
<td>Cu</td>
<td>324.75</td>
<td>3.82</td>
<td>5.56</td>
</tr>
<tr>
<td>Cu</td>
<td>327.40</td>
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<td>2.74</td>
</tr>
<tr>
<td>Cu*</td>
<td>327.98</td>
<td>5.42</td>
<td>0.13</td>
</tr>
<tr>
<td>Cu*</td>
<td>333.78</td>
<td>5.10</td>
<td>0.11</td>
</tr>
<tr>
<td>Cu</td>
<td>402.26</td>
<td>6.87</td>
<td>0.76</td>
</tr>
<tr>
<td>Cu</td>
<td>406.26</td>
<td>6.87</td>
<td>1.86</td>
</tr>
<tr>
<td>Cu</td>
<td>448.04</td>
<td>6.55</td>
<td>0.06</td>
</tr>
<tr>
<td>Cu</td>
<td>453.08</td>
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<td>6.19</td>
<td>4.50</td>
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<tr>
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<td>570.02</td>
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<td>0.0096</td>
</tr>
<tr>
<td>Cu</td>
<td>578.21</td>
<td>3.79</td>
<td>0.033</td>
</tr>
<tr>
<td>Zn*</td>
<td>307.21</td>
<td>4.03</td>
<td>0.013</td>
</tr>
<tr>
<td>Zn*</td>
<td>328.23</td>
<td>7.78</td>
<td>4.0</td>
</tr>
<tr>
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<td>7.78</td>
<td>18</td>
</tr>
<tr>
<td>Zn*</td>
<td>334.50</td>
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</tr>
<tr>
<td>Zn*</td>
<td>468.01</td>
<td>6.65</td>
<td>5.8</td>
</tr>
<tr>
<td>Zn*</td>
<td>472.22</td>
<td>6.65</td>
<td>15</td>
</tr>
<tr>
<td>Zn*</td>
<td>481.05</td>
<td>6.65</td>
<td>21</td>
</tr>
</tbody>
</table>
negative glow of a GRIMM discharge, some of these states are populated [112]. Therefore, for copper excitation in the jet-assisted plume, it appears that selective excitation is occurring at energies dictated by metastable collision-produced electrons.

The presence of recombination radiation from argon, the absence of argon ion radiation and selective excitation of sputtered species at energies close to the electron energy range for metastable collision-produced electrons support the existence of the equations shown in Fig. 5.6. However, it would be prudent to confirm these findings in other sputtered species.

A brass spectrum (60% Cu; 40% Zn), which has been obtained and presented under similar conditions to Figure 5.7, is shown in Figure 5.9. As one would expect, the relative intensities of the copper emission lines appear unchanged relative to the pure copper spectrum. Also, the only lines in the spectrum attributable to zinc and argon are atom lines, which resembles the response found in Fig. 5.7 for copper and argon.

Relative populations of the energy states for those transitions labelled with an asterisk in Figs 5.7 and 5.9 are shown in Figure 5.10. All relevant spectroscopic data for each transition are listed in Table VIII. Similarly to copper, a significant over-population of zinc energy states exists very near the energy range of the metastable collision-produced electrons. However, in this case, the zinc states are more energetic (7.78 eV) than the maximum electron energy limit by about 0.1 eV. This additional energy may be obtained in the kinetic energy of the metastable argon atoms as they collide, however. For a 1000 K plasma, each metastable atom would possess approximately this
Figure 5.9: Brass spectrum from 300 to 600 nm which has been corrected for the spectral response of the monochromator and PMT used. Emission lines designated with an asterisk are listed in Table VIII and used in Fig. 5.10. Discharge conditions used were similar to that used in Fig. 5.3 with the exception of discharge power: 25 W.
Figure 5.10: State distributions for copper and zinc in brass using emission intensities from Fig. 5.9: (□) - copper states; (●) - zinc states. I.P. of Cu refers to the first ionization limit for copper.
level of kinetic energy; therefore in a collision, it is possible that an additional 0.2 eV could be imparted to the produced electron. However, if these zinc levels are selectively excited, then why do the radiative copper energy states at 7.74 eV (Cu I 427.1, 465.11 and 529.25 nm) not display similar selective excitation? The answer to this question is that the copper states autoionize: they exist above the first ionization limit for copper and therefore do not relax by the spontaneous emission of radiation. Instead, the excited atom undergoes a radiationless transition to a state where it exists as an ion plus a free electron [94]. Therefore, these high energy states of copper are probably selectively excited by metastable collision-produced electrons, but since we are limited to verifying the event indirectly by examining the spontaneous emission from the state, it appears that they are not selectively excited.

In order for argon metastable atoms to be responsible for the excitation of sputtered atoms, one would expect that the behavior of both particles can be correlated as parameters, such as jet flow rate, are manipulated. From equation (5.1) in section 5.3.2, an increase in jet flow rate will produce a greater carrier gas velocity up the anode housing. A larger carrier gas velocity should be more effective in transporting long-lived species, like argon metastable atoms, from the negative glow to the jet-assisted plume.

5.3.5 Absorbance and Emission Measurements as a Function of Jet Flow Rate

HIEFTJE, RAYSON and OLESIK have examined excitation mechanisms in the ICP using a steady state approach [60]. They
argued that if the plasma exists as a steady state system, the concentrations of reactants and products are dictated by kinetically-controlled processes. This allowed a comparison of the spatial behavior of analyte emission intensities with the concentration product of reacting species. In their study, they used the similarity between the spatial map product of calcium ion and electron concentrations and the spatial emission intensity map for calcium I and II emission to provide evidence for the radiative ionization-recombination mechanism.

This same method can be used to evaluate the mechanism of analyte emission in the jet-assisted plume. Instead of comparing spatial maps, reactant and product behavior with increasing jet flow rate can be monitored. In jet-assisted glow discharge sources, jet flow rate has been shown to have a significant effect on analyte emission and absorbance [65]. Therefore, it would presumably have a significant effect on argon metastable atoms. The presence of the argon metastable atom in the jet-assisted plume is apparent in Figure 5.11. Significant absorbance of radiation at 811.5 nm is evident which corresponds to pumping the argon 4s[3/2]0 metastable level to the 4p[5/2] radiative level and there exists a definite increase in metastable population with increasing jet flow rate.

Recall that the production of analyte excitation is controlled by equations (5.6) and (5.7), namely:

$$\text{Ar}^m + \text{Ar}^m \xrightarrow{k_1} \text{Ar}^+ + \text{Ar} + e^-_{\text{fast}}$$
Figure 5.11: Absorbance signal for Ar I 811.5 nm as it varies with jet flow rate. Discharge conditions: constant voltage - 480 V, constant current - 52.0 mA; metered pressure was manipulated to maintain these constant conditions as the jet flow rate was changed.
If the reaction processes are kinetically-controlled, then the rate of excited analyte atom formation is given by:

\[
\frac{d[M^*]}{dt} = k_2 [M][e_{_{\text{fast}}}^-] - [M^*] A \tag{5.12}
\]

and the rate of fast electron formation is:

\[
\frac{d[e_{_{\text{fast}}}^-]}{dt} = k_1 [Ar^m]^2 - k_2 [M][e_{_{\text{fast}}}^-] \tag{5.13}
\]

If a steady state exists, then concentrations of excited analyte atoms and fast electrons will be invariant so that both these rates can be set to zero. As each equation contains the term \(k_2 [M][e_{_{\text{fast}}}^-]\), it follows that:

\[
k_1 [Ar^m]^2 = [M^*] A, \text{ or}
\]

\[
[M^*] \propto [Ar^m]^2 \tag{5.14}
\]

Therefore, if the collision of two metastable species is responsible for the production of fast electrons that excite analyte atoms, one would expect a strong correlation between the analyte emission and the
square of the argon metastable absorbance as the jet flow rate is changed.

Figure 5.12 represents the Cu I 406.26 nm emission intensity variation with jet flow rate on the left axis and the square of the Ar metastable absorbance under identical conditions on the right axis. The similarity between these two plots is obvious, each displaying similar variation with jet flow rate change. A correlation plot, where the square of the Ar absorbance is plotted against the Cu I emission intensity is shown in Fig. 5.13. The plot shows a high degree of correlation (correlation coefficient of 1.00) which provides strong evidence for metastable collision-produced electrons being responsible for the bulk of Cu I 406.26 nm emission. Table IX lists the correlation coefficients for various emission lines present in the jet-assisted plume. Each possesses a coefficient that approaches unity suggesting that metastable collision-produced electrons are responsible for their excitation also.

This argument could be strengthened by examining other reaction mechanisms and determining whether the degree of correlation is similar (it can not be realistically better for the emission lines tabulated) or worse than that found for metastable collision-produced electrons. If the correlation for other mechanisms proves worse, one would have a stronger argument that the dominant analyte excitation pathway in the jet-assisted plume is by collision of metastable argon atoms to produce a fast electron.

Another possible excitation mechanism that accounts for the selective excitation evident in Figs 5.8 and 5.10 is through radiative
Figure 5.12: Cu I 406.26 nm emission intensity and the square of the Ar I 811.5 nm absorbance versus jet flow rate: (○) - Cu I emission; (●) - square of Ar absorbance. Discharge conditions similar to those used for Fig. 5.11.
Figure 5.13: Correlation plot between the square of the Ar I 811.5 nm absorbance and the Cu I 406.26 nm emission intensity. Correlation of the straight line through the experimental points is 1.00.
Table IX: Correlation coefficients for metastable collision-produced electron excitation and radiative ionization-recombination excitation

<table>
<thead>
<tr>
<th>Emission Line (nm)</th>
<th>Correlation to $[\text{Ar}^m]^2$</th>
<th>Correlation to $[\text{M}][\text{Ar}^m]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu I 406.26</td>
<td>1.00</td>
<td>0.972</td>
</tr>
<tr>
<td>Cu I 324.75</td>
<td>0.998</td>
<td>0.963</td>
</tr>
<tr>
<td>Cu I 510.55</td>
<td>0.998</td>
<td>0.960</td>
</tr>
<tr>
<td>Cu I 521.82</td>
<td>0.989</td>
<td>0.936</td>
</tr>
<tr>
<td>Zn I 334.50</td>
<td>0.986</td>
<td>0.926</td>
</tr>
<tr>
<td>Zn I 481.05</td>
<td>0.990</td>
<td>0.932</td>
</tr>
</tbody>
</table>
ionization-recombination found in the ICP and examined by HIEFTJE et al. This mechanism involves the following reactions:

\[ M + Ar^m \xrightarrow{k_1} M^{++} + Ar + e^- \] (5.15)

\[ M^{++} \xrightarrow{A_2} M^+ + h\nu_{M^{++}} \] (5.16)

\[ M^+ + e^- \xrightarrow{k_2} M^* + h\nu_{\text{cont}} \] (5.17)

\[ M^* \xrightarrow{A_4} M + h\nu_M \] (5.18)

From these equations it is evident that the rate of formation of the excited analyte ion can be described by:

\[ \frac{d[M^{++}]}{dt} = k_1 [M][Ar^m] - [M^{++}] A_2 \] (5.19);

the rate of formation for the ground state analyte ion is:

\[ \frac{d[M^+]}{dt} = [M^{++}] A_2 - k_2 [M][e^-] \] (5.20);

and the rate of formation for the excited analyte atom is:

\[ \frac{d[M^*]}{dt} = k_2 [M][e^-] - [M^*] A_4 \] (5.21).
Again, if a steady state exists, then concentrations of these participants will be invariant so that each of these rates of formation can be set to zero. Using a series of substitutions, it can be shown that:

\[ [M^*] A_4 = k_1 [M][Ar^m], \text{ or} \]

\[ [M^*] \propto [M][Ar^m] \quad (5.22) \]

Therefore, if the radiative ionization-recombination mechanism is responsible for the excitation of analyte atoms, one would expect a strong correlation between the analyte atomic emission and the product of the argon metastable and ground state analyte atom concentrations as the jet flow rate is changed.

Figure 5.14 contains absorbance measurements for the copper ground state using resonance radiation at 324.75 nm as it changes with jet flow rate. These measurements indicate that the jets are quite efficient in transporting sputtered atoms to the jet-assisted plume: even flow rates as small as 10 cL/min can transport appreciable amounts of sputtered atoms to the analysis volume 25 mm from the sample surface. Little difference in the absorbance is apparent at jet flow rates between 30 to 90 cL/min, however.

It is interesting to note that the shape of this absorbance curve, indicative of the ground state population of copper atoms, is quite different to the shape for the sample loss rate versus jet flow rate (both obtained at similar conditions) published earlier [4] which demonstrated a continual increase in sample weight loss, although
Figure 5.14: Absorbance signal for Cu I 324.75 nm as it varies with jet flow rate. Discharge conditions similar to those used for Fig. 5.11.
with a diminishing slope, with increasing jet flow rate. Since atoms sputtered typically reside in the ground state, one would expect the shapes to be more comparable; however, the result suggests that the additional material removed from the sample surface at high jet flow rates is not transported to the jet-assisted plume, but is likely deposited on the walls of the anode housing during transit.

The correlation plot in Fig. 5.15 for Cu I 406.26 nm emission intensity variation with jet flow rate on the abscissa and the product of the Ar metastable and Cu atomic ground state absorbances under identical conditions on the ordinant axis demonstrates that the degree of similarity between these two variables is considerably worse relative to that found for the Cu I 406.26 nm emission intensity and square of the Ar metastable absorbance. The correlation coefficient was calculated to be 0.9718. Table IX also contains the correlation coefficients for other emission lines measurable in the jet-assisted plume using the product of the Ar metastable and Cu atomic ground state absorbances. In each case, the correlation coefficient is significantly better for the metastable collision-produced electron mechanism indicating that this is more likely the correct excitation pathway. Furthermore, if the radiative ionization-recombination mechanism is responsible for the excitation of analyte atoms, one would anticipate seeing significant analyte ion emission in the jet-assisted plume through the PENNING process shown in equations (5.15) and (5.16). However, no trace of analyte ion emission is evident in the collected spectra (Figs 7 and 9) with the exception of the Cu II emission line attributable to charge transfer between the
Figure 5.15: Correlation plot between the product of the Ar I 811.5 nm and Cu I 324.75 nm absorbances and the Cu I 406.26 nm emission intensity. Correlation of the straight line through the experimental points is 0.972.
copper ground state atom and an argon ion in a metastable state in close proximity to the ionic ground state.

There is, of course, another possible atomic excitation pathway which involves electron impact with the fast electrons being produced from the electric field - as in the negative glow. If this were the case, then the rate of fast electron formation would be dependent on the electric field strength as well as the extent of analyte excitation. However, according to HIEFTJE et al., the relationship:

$$[M^*] \propto [M][e^-] \tag{5.23}$$

will hold for electron impact excitation [60]. Unfortunately, we possess no data for electron density in the jet-assisted plume and how it varies with jet flow rate so the correlation between the excited analyte atomic emission and the product of the analyte ground state atomic absorbance and electron density could not be verified. However, it should be noted that differentiation between this mechanism and that involving metastable collision-produced electrons would not be possible using this exercise since equation (5.22) also holds for the latter mechanism.

5.4. Summary

Radially-resolved surface and topographic maps depicting atomic emission intensity in the jet-assisted plume show a marked invariance to emission line type with regard to the relative distribution of emission for two analyte lines and one support gas line. The axial emission does decay exponentially, although the decay is not due to
the natural lifetime of the transition as each of the three lines demonstrated similar decay as a function of axial distance. This indicates that the observed decay is probably due to the decay of the exciting medium.

The jet-assisted plume more closely resembles a flowing afterglow as opposed to an extension of the negative glow. Energy transfer from the negative glow to the plume could be carried out by argon metastable atoms: the collision of two argon metastable atoms in the plume could ionize one of the atoms and produce an energetic electron (energy equal to the difference between the sum of the metastable energies and the first ionization potential of argon: 7.32 - 7.68 eV) capable of exciting atomic transitions.

The atomic state distributions for copper and zinc support the premise that selective excitation was occurring at the energy purported for argon metastable collision-produced electrons. Furthermore, the correlation in behavior between analyte atomic emission and the square of the argon metastable absorbance as jet flow rate is manipulated, provides strong evidence for the argument that the excitation of analyte atoms occurs by metastable collision-produced electrons.
CHAPTER 6

COMPARISONS BETWEEN A GRIMM-TYPE GLOW DISCHARGE
AND BOTH AN AXIALLY AND LATERALLY VIEWED JET-ASSISTED
GLOW DISCHARGE

6.1 Introduction

Although glow discharges can directly analyze solid samples, the sputtering process is tempered by the re-deposition of sputtered material which attenuates the sampling efficiency [18]. This problem has been addressed by the Analyte Corporation's ATOMSOURCE™ [14] and the sampling efficiency of a similar design, with regard to re-deposition reduction, has been the subject of an investigation pursued in Chapter 4. Both the ATOMSOURCE™ and discharges modelled on its design have been the subject of scientific scrutiny [2, 3, 23, 32-34, 55, 65, 69-71, 87, 106, 118, 119]. The ATOMSOURCE™ has been described in Chapter 1; however, a short description on its similarities and differences to other glow discharges is useful at this point. The ATOMSOURCE™ is familiar in that it uses the basic hollow anode of the GRIMM glow discharge brought to within a mean free path of the cathode to form an obstructed discharge [18]. However, it differs from the GRIMM design by the use of six jets, arranged in a hexagonal pattern around the inner circumference of the anode, which direct support gas at the sample surface. It has been demonstrated that the use of jet-assisted support gas flows significantly increase sample ablation rates relative to a GRIMM-type glow discharge [2, 23] largely through a reduction in re-deposition [4].
Despite the increase in ablation rate, the emission intensities of some sputtered atom lines decrease with increasing jet flow rate [2, 3, 23, 65]. These diminishing signals only occur for emission lines with appreciable absorption coefficients. It was found that the jets produce an increase in absorption path length invoked by the entrainment of sputtered atoms along the optical axis of the source which can lead to self-absorption [3].

An obvious remedy to this problem is to rotate the optical axis 90° so that the absorption path length is reduced. It has been shown that the lateral width of the jet-assisted plasma plume is significantly less than the axial length [6]. However, in rotating the axis, emission from the negative glow is obstructed: only the jet-assisted plume can be analyzed and at axial distances no closer than 25 mm from the sample surface with the present source geometry. Therefore, one would expect that a reduction in signal intensity would result from lateral-viewing which could lead to a decline in analytical performance relative to axial-viewing.

The purpose of this study is to compare lateral- with axial-viewing with regard to analytical performance. In addition, the reduction in self-absorption, actuated by the optical axis rotation, will be examined.

6.2. Experimental

The jet-assisted glow discharge source used in this study has been described elsewhere [4, 6]. Nonetheless, Figure 6.1 contains schematics of the source which demonstrate axial-viewing (Fig. 6.1a) and lateral-viewing (Fig. 6.1b). If there exists no support gas flow
Figure 6.1: Schematic diagram of the jet-assisted glow discharge source displaying a) axially viewed and b) laterally viewed emission from the jet-assisted plasma plume.
through the jets, then the jet-assisted source becomes a GRIMM-type glow discharge. When lateral-viewing, the side pumping port used when axial-viewing, remains closed: no additional vacuum pumping is used.

Emission spectra were collected by the same system described in Chapter 5. Line shapes were obtained using the method described earlier in Chapter 3. Calibration curves presented in this manuscript contain data that have been published previously [3]; the lateral-viewed calibration curve was obtained using the same monochromator and linear photodiode array.

Signal standard deviations at different jet flow rates were obtained by the following procedure. The emission line was monitored for 10 sec for any one jet flow rate and an average signal determined. This process was repeated five times to achieve five averaged signals for each jet flow rate investigated. The standard deviation of the five averaged signals was then reported as the signal standard deviation.

Limits of detection for copper using the Cu I 521.82 nm emission line for the three types of glow discharge source were obtained using similar discharge conditions: constant voltage, constant current (600 V, 50 mA); and similar equipment settings. The background and background RSD was obtained by setting the monochromator to a wavelength of 521.5 nm and sampling the background signal for 10 seconds at a rate of 10 Hz using a current amplifier setting which was two orders of magnitude larger than that used to acquire the Cu I signal. An average background signal and its RSD was calculated from the resulting 100 points.
6.3. Glow Discharge Comparisons

6.3.1 Copper Spectra

Figure 6.2a contains a copper spectrum obtained using no support gas flow through the jets, viewed axially. When used in this mode, the jet-assisted glow discharge source emulates a GRIMM glow discharge. From this point on in the Chapter, the zero jet flow rate case will be referred to as a GRIMM-type glow discharge. The spectrum displays significant resonance line emission at 324.75 and 327.40 nm as well as prominent green lines at 510.55, 515.32 and 521.82 nm. The second order Cu II 224.70 nm emission line is also prominent in the spectrum at a wavelength of 449.40 nm due to a charge transfer reaction between the copper ground state atom and a metastable argon ion [98]. Also evident is Ar II emission (i.e. in the vicinity of 350 nm) indicative of very fast electrons which have achieved sufficient energy for support gas ion excitation through acceleration in the cathode dark space [30].

In Figure 6.2b, a similar copper spectrum (axial-viewing) is shown with the exception of jet flow rate which has been increased to 30 cL/min. It is apparent that the relative intensities of some emission lines has changed and that the emission intensity scale for the spectrum has increased. The self-absorption of the resonance lines is apparent by comparing the relative intensities in Figs 6.2a and 6.2b: the resonance lines possess smaller intensities at the greater jet flow rate. Other emission lines, however, demonstrate increases in intensity with the larger jet flow rate: both the Cu II and the green lines
Figure 6.2: Copper spectra corrected for the spectral response of the detection system used (power: 25 W, pressure: 2.9 mbar): a) GRIMM-type glow discharge; jet-assisted glow discharge, 30 cL/min: b) axially viewed; c) laterally viewed.
show increases by a factor of about 3. The increasing green line intensities explain the green hue of the jet-assisted plume when copper is used as a cathode. Furthermore, the Cu I 402.26 and 406.26 nm lines show increases in intensity by a factor of five. Conversely, Ar II and Ar I emission at 415.86 and 420.02 nm appears unchanged in intensity, in agreement with past findings [49], for the two cases which suggests that the use of jets increases sampling rather than excitation efficiency.

Figure 6.2c shows a copper spectrum obtained at similar conditions to Fig. 6.2b except viewing is laterally: only the jet-assisted plume can be sampled using this optical axis. The first obvious difference between this spectrum and Figs 6.2a and 6.2b is the intensities of the emission lines which are typically an order of magnitude less intense. Also, the absence of any Ar II emission indicates that the ionizing plasma typically associated with the negative glow is no longer being sampled. Although the resonance lines have been restored as the most intense lines in the spectrum, their relative intensity to the Cu I 402.26 and 406.26 nm lines is much smaller than in Fig. 6.2a: for example the ratio between Cu I 324.75 and Cu I 406.26 nm in Fig. 6.2a is about 8; in Fig. 6.2c, this ratio is less than 3. At face value, this suggests that the self-absorption problem associated with using appreciable jet flow rates has been reduced but not eliminated. The Cu II 224.70 and Cu I 510.55 nm emission lines also demonstrate an intensity reduction relative to other emission lines in the spectrum. However, the Cu II line emission intensity relative to other lines is restored by increasing the jet flow rate; but the green line remains diminished relative to other lines regardless of
what jet flow rate is used [6]. This behavior is also evident for the other two emission lines at 570.02 and 578.21 nm which similarly decay to the low-lying copper metastable levels (1.39 and 1.64 eV). This relative reduction in emission intensity suggests that these low energy states are not as efficiently excited in the jet-assisted plume relative to the negative glow which supports the belief that excitation in the jet-assisted plume is dominated by metastable collision-produced electrons that are introduced into the plume by the metastable collision cycle at energies between 7.32 to 7.68 eV [6].

For this supposition to be true, the resonance lines should demonstrate a similar reduction in relative intensity when viewed laterally since all five emission lines are produced through spontaneous emission from the 3d$^{10}$4p states (either $^2P_{3/2}$ or $^2P_{1/2}$). This may explain the relative intensity difference between the resonance lines and the Cu I 406.26 nm emission line evident in Figs 6.2a and 6.2c. In the jet-assisted plasma plume, the width of visible emission in the lateral direction is about an order of magnitude less relative to its length in the axial direction at a jet flow rate of 30 cL/min, so one would expect that the reduction in absorption path length in viewing laterally would substantially reduce if not eliminate self-absorption. To determine whether self-absorption or the selective excitation of high energy states by the metastable collision cycle is responsible for the reduction in relative intensity originating from the 3d$^{10}$4p states and that from the 3d$^{10}$5d states of Cu I 402.26 and 406.26 nm in Figs 6.2a and 6.2c, line shapes of the Cu I 324.75 nm emission line can be examined for line shape broadening attributable to self-absorption [3].
6.3.2 Evaluation of Self-absorption

Figure 6.3a shows the line shapes of the resonance line using a jet flow rate of 30 cL/min for both axial- and lateral-viewing. It is evident that the line shape for the lateral-viewed case is significantly narrower than the axial case. This is also true for comparisons with a GRIMM-type glow discharge with resonance line emission collected axially (Fig. 6.3b): the lateral-viewed emission line displays a significantly narrower line shape, despite the use of a 30 cL/min jet flow rate. It has been shown previously that this is not due to pressure broadening [3], therefore it appears that through lateral-viewing of the jet-assisted plume, self-absorption can be significantly reduced relative to even a GRIMM glow discharge which has been shown to suffer from self-absorption at certain conditions previously [115]. Furthermore, Figure 6.3c demonstrates that an increase in jet flow rate from 30 to 90 cL/min produces no measurable difference in line shape for the resonance line provided the jet-assisted plume is viewed laterally. This indicates that there is little lateral spread of sputtered atoms invoked by increasing the jet flow rate. Therefore, the absorption path length remains unchanged producing no increase in self-absorption.

It appears that by viewing the jet-assisted plume laterally, self-absorption has been reduced relative to using no support gas flow through the jets. These findings support the premise of selective excitation of high energy states by the metastable collision cycle. Low lying levels, like the 3d^{10}4p states of copper are relatively underpopulated relative to higher lying states, like the 3d^{10}5d states
Figure 6.3: Cu I 324.75 emission line shape comparisons (power: 30W): a) 30 cL/min, 3.3 mbar: (●) - axially viewed, (□) - laterally viewed; b) 3.3 mbar: (●) - GRIMM-type glow discharge, (□) - laterally viewed at 30 cL/min; c) laterally viewed: (●) - 90 cL/min, 4.7 mbar, (□) - 30 cL/min, 5.7 mbar.
provided the energy of the upper state does not exceed the upper energy limit for metastable collision-produced electrons.

6.3.3 Relative Sensitivity and Precision

Figure 6.4a displays the variation in Cu I 521.82 nm emission signal viewed axially and the signal standard deviation as the jet flow rate is changed. It is apparent that although the signal increases with increasing jet flow rate, so does its standard deviation. However, the increase in signal standard deviation is not as significant as the gain in signal strength up to 20 cL/min, so that an optimum precision, expressed as a %RSD is available using a jet flow rate of 20 cL/min when viewing axially (Fig. 6.4b). This constitutes a gain in precision by about a factor of 2 relative to a GRIMM-type glow discharge which is represented at the y-axis (0 cL/min jet flow rate). This improvement is rather questionable, however, since the error associated with the evaluation of the precision nearly spans this difference.

Figure 6.5a repeats the experiment shown in Fig. 6.4a, except using lateral-viewing. It is apparent that the relative sensitivity, expressed on a relative scale from the current-amplified PMT output, is about an order of magnitude smaller when viewing laterally relative to axially, provided the same jet flow rate is used. This magnitude is reduced, however, if larger jet flow rates are used when viewing laterally. Flow rates greater than 30 cL/min can not be used when viewing axially with the present design due to deposit of sputtered material on the optical window. The signal standard deviation is also substantially reduced when viewing laterally so the resultant %RSD is approximately the same as for a GRIMM-type glow discharge (Fig.
Figure 6.4: Sensitivity and precision for axial viewing of Cu I 521.82 nm emission intensity (power: 25 W, pressure: 3 mbar): a) (●) - signal intensity, (□) - signal standard deviation; b) %RSD in signal intensity.
Figure 6.5: Sensitivity and precision for lateral viewing of Cu I 521.82 nm emission intensity (power: 25 W, pressure was set by the flow of support gas through the jets: 2.9 - 5.2 mbar for 30 - 90 cL/min):

a) (●) - signal intensity, (□) - signal standard deviation;
b) %RSD in signal intensity.
6.5b). In addition, the signal standard deviation closely follows the signal, therefore little change in %RSD is seen with increasing jet flow rate.

For all types of glow discharge, the %RSD of the signal is impressive: at any flow rate the precision is approximately 0.3 %. In addition, the signal standard deviation appears to follow the signal as the jet flow rate is manipulated indicating that the dominant noise source in the plasma is flicker noise.

6.3.4 Calibration Curves

It has already been established that the use of resonance lines when axial-viewing may be precluded if the transition possesses a large absorption coefficient due to the self-absorption of the emission line [3]. Figure 6.6 contains three nickel calibration curves using the Ni I 352.45 emission line. The axial-viewed jet-assisted glow discharge, using a jet flow rate of 30 cL/min, displays roll-over indicative of self-absorption; whereas the other two, a GRIMM-type glow discharge and a lateral-viewed jet-assisted glow discharge, using a jet flow rate of 50 cL/min, display linear curves over the concentration range studied. In addition, this study in Section 3.2 has shown that the degree of self-absorption is measurably less for lateral-viewing of a jet-assisted glow discharge relative to the GRIMM-type glow discharge. Therefore, one may expect that the dynamic range for glow discharge atomic emission analyses may be extended by using a lateral-viewed jet-assisted glow discharge.
Figure 6.6: Nickel I 352.45 nm calibration curves (discharge power: 25 Watts): (●) - GRIMM-type glow discharge, 9 mbar; (□) - Axial viewed jet assisted glow discharge, jet flow rate: 30 cL/min, 9 mbar; (▲) - Lateral viewed jet assisted glow discharge, jet flow rate: 50 cL/min, 4.2 mbar.
6.3.5 Limits of Detection

Boumans and co-workers have recently demonstrated the use of a new method for calculating limits of detection that permit relative comparisons of different optical spectrometers [20]. In this approach, the Limit of Detection (LOD) is given by the equation:

$$\text{LOD} = \frac{0.03(RSDB)m}{(SBR)}$$

(6.1)

where RSDB is the relative standard deviation in the background, m is the concentration of analyte used in the determination, and SBR is the signal to background ratio. The background should be obtained using a blank sample at the same wavelength as the signal, however, this presents a problem when using solid-sampling glow discharges: it is difficult to obtain a conducting, solid blank. For this reason, it has been decided to use a point on the spectrum in close proximity to the selected copper emission line at 521.82 nm which displays no measurable emission intensity at the same current amplifier gain setting. This may preclude comparison with other glow discharge spectrometers, but it does allow comparison between axial- and lateral-viewing for the jet-assisted glow discharge source. Table X contains the parameters used in calculating the LOD using a sample of commercial grade copper (taken to be 99 % Cu). The detection limit reported here using a GRIMM-type glow discharge is within an order of magnitude of those reported elsewhere [22] for different elements providing an adequate benchmark to make our comparisons.
Table X: Copper limits of detection for a GRIMM-type and both an axially viewed and laterally viewed jet-assisted glow discharge source.

<table>
<thead>
<tr>
<th>Figure of Merit</th>
<th>GRIMM-type</th>
<th>Axial Jet 30 cl/min</th>
<th>Lateral Jet 30 cl/min</th>
<th>Lateral Jet 90 cl/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limit of Detection (ppm)</td>
<td>8</td>
<td>4</td>
<td>50</td>
<td>7</td>
</tr>
<tr>
<td>Signal (a.u.)</td>
<td>2302</td>
<td>5310</td>
<td>47.8</td>
<td>550</td>
</tr>
<tr>
<td>Background (a.u.)</td>
<td>1.44</td>
<td>1.82</td>
<td>0.123</td>
<td>0.179</td>
</tr>
<tr>
<td>%RSD Background</td>
<td>0.443</td>
<td>0.443</td>
<td>0.641</td>
<td>0.709</td>
</tr>
</tbody>
</table>
When axially viewing, the LOD is reduced by a factor of two using a jet flow rate of 30 cL/min relative to a GRIMM-type glow discharge. This is due largely to an increase in sampling efficiency, but an increase in the background signal compromises the result somewhat. In comparing a GRIMM-type glow discharge to a laterally viewed glow discharge using a jet flow rate of 90 cL/min, no real difference is seen in the LOD. This equality is due to the balance between 1) an increased sampling efficiency coupled with a large reduction in background signal and 2) poorer transport efficiency to the viewing zone at an axial distance of 25 mm from the sample surface coupled with a larger RSDB for the lateral case. Using a jet flow rate of 30 cL/min in conjunction with lateral viewing, transport efficiency is further reduced and any improvement in RSDB or reduction in background is insufficient to produce an LOD comparable to the 90 cL/min case. If the pressure is reduced such that the jet flow is allowed to set the source pressure while maintaining the same power level (as in Fig. 5), transport efficiency using a jet flow rate of 30 cL/min is improved so that the signal intensity is increased when laterally viewing, but this is achieved at the cost of an increase in RSDB to the extent that the LOD is only marginally improved.

6.4. Summary

Table XI compares the analytical figures of merit determined in this study for each of the three glow discharges investigated: a GRIMM-type and both an axial-viewed and lateral-viewed jet-assisted glow discharge. Choice for a particular glow discharge appears to
depend upon application. If limit of detection is a motivating factor, then an axial-viewed jet-assisted glow discharge appears to be the best choice. However, if multi-element analysis is required, then the lateral-viewed jet-assisted glow discharge may be the best choice since it should provide the largest linear dynamic range and a relative freedom from spectral interferences due to an inherently simpler spectrum without much sacrifice in detection power. It should be noted, however, that the GRIMM-type glow discharge provides excellent all-round performance.
Table XI: Comparison of figures of merit for a GRIMM-type and both an axially viewed and laterally viewed jet-assisted glow discharge source.

<table>
<thead>
<tr>
<th>Figure of Merit</th>
<th>GRIMM-type</th>
<th>Axial Jet-Assisted, 30 cl/min</th>
<th>Lateral Jet-Assisted, 90 cl/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limit of Detection</td>
<td>+</td>
<td>* / +</td>
<td>+</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>+</td>
<td>*</td>
<td>-</td>
</tr>
<tr>
<td>Dynamic Range</td>
<td>+</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td>Precision</td>
<td>+</td>
<td>* / +</td>
<td>+</td>
</tr>
<tr>
<td>Background</td>
<td>-</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td>Spectrum Simplicity</td>
<td>+</td>
<td>-</td>
<td>*</td>
</tr>
</tbody>
</table>

Note:  * - best performance  
+ - next best performance  
- - worst performance
CHAPTER 7

CONCLUSIONS

7.1 Generalities

Most analytical instrumentation based on the detection of atomic emission performs the dual role of atomization and excitation of the analyte. Therefore, these emission sources can be investigated from two vantage points: one dealing with the atomization of the analyte; the other with its excitation. This is certainly true of the jet-assisted glow discharge source. An effort has been made in this thesis to investigate and understand both atomization and excitation processes occurring in this source and how they relate to other, more popular instrumentation. This Chapter is intended to summarize the important findings of this work.

In addition, future investigative directions will be indicated which should lead to the enhancement of the analytical performance of the jet-assisted glow discharge source relative to its demonstrated ability in the preceding Chapters.

7.2 Atomization

Initial studies carried out on the atomization characteristics of the jet-assisted glow discharge indicated that the amount of sample material removed during sputtering could be increased by a factor of three when using a flow of argon through the jets greater than 20 cL/min, relative to a GRIMM-type glow discharge, at a similar power and pressure. Later studies indicated that this was not due to an
increase in the sputtering rate, but to a reduction in the re-deposition of sputtered material onto the sample surface. This re-deposition reduction is principally located on the burn spot where the support gas flow impinges resulting in the formation of craters on the sample. The crater formation attests to the non-uniform atomization conditions occurring at the sample surface. This effectively precludes the practical application of depth profiling which relies on the uniform layer-by-layer removal of material, obtainable with static glow discharges, to characterize the sample for its elemental composition as it varies with depth.

The turbulence at the sample surface caused by the mixing of gas from the six jets produces a greater distribution of positive ion incidence angles as they are accelerated towards the cathode by the electric field. This tends to impede the formation of symmetrical surface structures like cones and hillocks found on the burn spots of static discharges. According to some researchers [69], this may lead to a reduction in preferential sputtering and matrix effects.

7.3 Excitation

A major consequence of using jets to increase the sampling efficiency with the present design of jet-assisted glow discharge source is that sputtered atoms are entrained along a path following the surface normal. The original design incorporated a line of observation which was co-axial with the surface normal in keeping with the GRIMM-type design (axial-viewing). Since the majority of sputtered atoms exist in the ground state, the entraining of atoms along the line of observation caused by the jet flow rate resulted in a
significant increase in the absorption path length precipitating a self-absorption problem for emission lines with appreciable absorption coefficients. This prevented the use of some of the most sensitive emission lines if their parent element was of significant concentration in the sample.

An obvious remedy to this problem is to rotate the line of observation thereby reducing the absorption path length. However, in doing so, the sample surface can no longer be viewed and only the plasma plume issuing from the anode housing can be analyzed which is 25 mm from the sample surface. This lateral-viewed plasma plume has been shown to be a flowing afterglow rather than an extension of the negative glow. It is sustained by energy transport from the negative glow by argon atoms residing in metastable states. The collision of two argon metastable atoms in the plume produces an electron capable of excitation to states of energies up to approximately 7.9 eV. Since most samples sputtered tend to contain transition metals, little ionization occurs in the plume; rather atomic excitation is the primary cause of light emission in the plume.

Both axial- and lateral-viewing offers advantages over the GRIMM-type glow discharge. Axial-viewing provides greater detection power, although at the expense of dynamic range and spectrum complexity. Lateral-viewing provides similar detection power to a GRIMM-type glow discharge with the possibility of greater dynamic range and spectrum simplicity.
7.4 Future Directions

At present, lateral-viewing is limited to a line-of-sight emission intensity measurement which is 25 mm from the sample surface. This displacement from the negative glow severely reduces the sensitivity of emission measurements; however, detection power is retained relative to a GRIMM-type glow discharge due to a concomitant reduction in background signal. The exponential decay of the plasma plume emission as it issues from the anode housing suggests that an enhancement in sensitivity can be achieved with lateral-viewing closer to the cathode surface. This increase in sensitivity should not be compromised by a similar increase in background evident with axial-viewing. Therefore, an increase in the signal to background ratio would produce lower detection limits than those reported in this thesis. This, coupled with large dynamic range and spectrum simplicity, should make the lateral-viewed jet-assisted glow discharge source more attractive for quantitative analyses of solid, conducting samples.

A new design for the jet-assisted glow discharge source has been proposed and appears in Figure 7.1. This design incorporates several modifications intended to improve the analytical performance relative to previous models. This includes a larger pumping port orifice and auxiliary support gas inlets positioned such that turbulence in the plasma plume is reduced. In addition, support gas is individually fed to each of the four jets which should produce a more uniform burn spot. The most important modification, however, is that lateral-viewing of the plasma plume is possible only 10 mm from the sample surface. As indicated in the preceding paragraph, this
Figure 7.1: Schematic of the jet-assisted glow discharge source which has been modified to allow lateral viewing of the plasma plume at approximately 10 mm from the sample surface.
should result in a significant increase in the detection power of the jet-assisted glow discharge source.
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