AQUEOUS SOLUTION SAMPLING AND THE EFFECTS OF WATER VAPOR IN GLOW DISCHARGE MASS SPECTROMETRY

By

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This work is dedicated to my parents, whose love and support helped me get through my many years of education.
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Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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By

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Chairman: Willard W. Harrison
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Glow discharge mass spectrometry is an accepted technique for the analysis of trace elements in solid materials. In this dissertation, the sampling of small volume aqueous solution samples has been explored. This method uses electrothermal vaporization of a solution residue for atomization, while a glow discharge provides the excitation and ionization. The main advantage of this technique over other glow discharge solution analysis schemes is the increase in sensitivity for a given sample since the analyte is atomized in a short time. The effects of the electrothermal filament current on the plasma processes were studied, since this could influence the discharge processes as well as ion transport to the mass spectrometer. Variables such as pressure, cathode-to-exit orifice distance, atomization current, and sample placement on the cathode were evaluated and the best parameters presented. The method was found to have relative standard deviations between 15-20 %. Multi-element samples may be
analyzed using either mass spectral scanning or separation of the elements by their vaporization temperature. The biggest disadvantage of this method is the irreproducibility, which is attributed to the introduction of contaminant gases with each sample.

The effects of water vapor on the processes of the glow discharge were also investigated. This is important since water vapor is always present in the ion source to some extent. Water vapor exhibits detrimental effects on both atomization and ionization in the plasma. Mass spectra taken with less than 5% water vapor resulted in ion signals primarily from $\text{H}_2\text{O}$, $\text{H}_3\text{O}$, ArH, and $\text{O}_2$. This is due to ion molecule reactions and water dissociation occurring in the plasma. A liquid nitrogen coil was constructed to aid in the removal and control of water vapor in the ion source. Mass spectra obtained while cooling the source contained ion signals mainly from the cathode material. Different cathodes were investigated to observe the varying effects of the water vapor. It was found that when sputtering reactive metals (such as getters) the water problem may be minimized. Both steady state and pulsed addition of water were examined to determine the processes occurring in the plasma.
CHAPTER 1
GLOW DISCHARGE MASS SPECTROMETRY

Introduction

The glow discharge is an old source that has been used over the years primarily for applications that benefit from conversion of a solid sample into atoms, ions, and photons that are characteristic of the sample's content. Glow discharge devices have been constructed in a variety of configurations and have shown promise in many applications ranging from optical spectroscopy to mass spectrometry. The earliest reported works examined using the glow discharge for optical spectroscopy, with one of the first publications appearing in 1916 by Paschen [1]. Aston [2] used the glow discharge source in the 1940's for its ion production ability. This source aided Aston's experiments to evaluate and develop the technique of mass spectrometry, which was then in its infancy.

The majority of the studies reported in this dissertation use mass spectrometry to sample the ion population produced by a glow discharge source. Optical methods, such as atomic absorption (AA) and atomic emission (AE), were also performed in some instances to obtain complementary data on the atomic population of both ground state and excited species that coexist with ions in the plasma. The results obtained in these experiments help provide an insight into the fundamental processes occurring in the glow discharge plasma as well as
give some indication to the types of analytical studies that may be conducted and the considerations that must be made when using this source.

General Description of Gaseous Discharges

Gaseous discharges are obtained upon establishing a flow of electric current through a gaseous medium [3]. Gas discharges may be classified according to the current with which they operate. Figure 1 shows a schematic representation of the characteristics of gaseous discharges with respect to their voltage and current [4]. There are generally considered to be at least three types of discharges: 1) the Townsend discharge, 2) the glow discharge, and 3) the arc discharge. The Townsend discharge operates at very low currents, which give rise to its nonluminous appearance, since the population of excited species that provide a discharge with its bright appearance is at very low concentrations. The Townsend discharge is not self-sustaining and requires external phenomena such as X-rays or UV light that will produce electrons in the gas to aid in ion production. A Townsend discharge for analytical mass spectrometry has been used [5] to ionize the reagent gas rather than high energy electrons emitted from a hot filament. The central sections of Figure 1 comprise the areas of glow discharge operation (both normal and abnormal). Abnormal glow discharges are used in the studies presented here and will be further explained below. The final section is the area in which an arc discharge operates. The arc discharge has a very intense luminosity and operates at very high currents, where thermionic emission from the cathode provides the electrons for this source. This type of
Figure 1 The relationship between voltage and current in a gaseous discharge [4]. $V_b$: breakdown voltage, $V_n$: normal cathode fall potential, $V_d$: arc voltage.
discharge has found use for analytical spectrographic emission [6] and for the vapor deposition of thin films [7].

The basic schematic of a glow discharge system is shown in Figure 2. The main requirements for glow discharge operation are shown in the figure. The requirements include a low pressure inert gas atmosphere (most often argon), a cathode (usually the sample to be analyzed), an anode (usually the glow discharge source housing), and a power supply to provide the high voltage to the cathode. The dc/pulsed power supply develops a potential difference between the cathode and the anode, which are both in contact with the low pressure inert gas. In the dc mode, the power supply provides a constant voltage to the cathode, while in the pulsed mode the discharge is switched on and off rapidly with a given frequency. Upon application of the voltage, free electrons that exist in this low pressure gaseous environment will accelerate toward the anode, which has a positive bias due to the potential gradient that exists in the chamber. As these electrons pass through the gas, they collide with and sometimes ionize the gaseous species. Positive ions are created and accelerate toward the cathode, which has a negative bias. As the gas ions strike the cathode a variety of species is liberated, such as neutral atoms and molecules, ionized atoms and molecules, electrons, and photons. The emitted electrons will accelerate toward the anode and complete the electrical circuit. With this flow of electrons, the discharge will maintain a continuous flow of current and be self-sustaining. The pressure regime that may be used to operate a glow discharge is from about 0.1 - 10 Torr.
Figure 2  Schematic of a glow discharge circuit showing the primary regions of the plasma.
Discharge formation at these pressures requires a potential of 500 - 2000 V, which results in a current in the low milliamp range.

The glow discharge is one type of plasma that is used for analytical studies. A plasma is a partially ionized gas volume that consists of a generally equal concentration of positively and negatively charged species, as well as a large number of neutrals. The glow discharge contains a variety of zones that are evident from Figure 2. These different zones have been characterized with respect to their light intensity, potential distribution, field strength, space charge, negative and positive charge regions and the negative current density [8]. The layers that are present in the glow discharge (from the cathode to the anode) are the Aston dark space, the cathode layer, the cathode dark space, the Faraday dark space, the positive column, the anode dark space, and the anode glow. For all of the regions to be noticeable the anode-cathode distance must be of sufficient length. In commercial neon lights, the emission that is viewed is from the positive column, not the negative glow shown here. For the GDMS ion source the regions from the Faraday dark space out to the anode are missing due to the close proximity of the anode to the cathode. Also, the Aston dark space that is near the cathode is not visible because it is surrounded by the cathode glow, which appears to "coat" the cathode since it is so close to its surface. The analytically significant processes for GDMS operation occur in the cathode dark space and the negative glow regions of the discharge, so the discussions here will only refer to those regions. These regions are named "dark" and "glow" according to the relative presence or absence of luminosity caused by the
radiative relaxation occurring in these regions [9]. The cathode dark space is
dark because there is very little emission from the electron-atom collisions that
occur here, due to the electrons that have been accelerated by the cathode
potential and can no longer sufficiently ionize the discharge gas [10]. In the
negative glow region, however, excitation and ionization will occur. The primary
color of the negative glow is a result of the light emitted upon the radiative
relaxation of the discharge gas. Argon glow discharges are normally a light blue
color, while the emission from neon is red in color.

As previously mentioned, and shown in Figure 1, there are two operational
regimes for a glow discharge: a normal and abnormal cathode fall. In a normal
glow discharge there is a constant increase in current even as the applied voltage
remains steady. The increasing current is compensated for by a subsequent
increase in the area of the cathode that is surrounded by the negative glow
region. Thus the current density, the amount of current for a given area of the
cathode, remains constant [3]. Once the complete cathode area is covered by
the negative glow, any further increase in current requires an increase in the
current density and thus an increase in the discharge potential. This mode is
called an abnormal discharge and is the mode that is almost always used for
analytical glow discharge devices because it is the most stable form. All studies
described in this dissertation used an abnormal glow discharge ion source.

Types of glow discharge devices

The sample to be analyzed is made to be the cathode in the electronic
circuit, while the anode can be constructed of any material. The ion source
chamber housing serves as the anode in the mass spectral studies described in this dissertation. This particular type of glow discharge configuration is called a coaxial cathode glow discharge. Other types of glow discharges include: 1) the planar diode, 2) the hollow cathode, 3) the Grimm discharge lamp [11], and 4) the hollow cathode plume. These configurations are shown in Figure 3.

**Coaxial cathode.** This cathode is illustrated in Figure 3A and the majority of the GDMS work that has been done uses this type of cathode. This is due to the ease of using the ion source chamber of the mass spectrometer as the anode. Samples for this type of glow discharge are in the form of a 1 - 2 mm diameter pin with about five millimeters left exposed to the plasma, or a pressed disk that is shielded to allow only the top surface of the sample to be exposed to the plasma. Conducting, bulk samples can be machined into the pin form directly, while powders (conducting and nonconducting) are pressed into the disk form. The nonconducting samples must be mixed with a conducting powder before pressing unless an rf power supply is used. When using rf, care must be employed to assure that sputtering is localized to the target area of the electrode.

**Planar diode.** This is the simplest configuration (shown in Figure 3B) that is used analytically and may also be operated with either dc or rf voltage. Planar diode glow discharges using an rf power supply were used by Coburn et al. for mass spectrometry studies of the ion population present in sputter deposition plasma chambers [12].

**Hollow cathode.** The hollow cathode lamp, shown in Figure 3C, is probably the most familiar glow discharge that is used in chemical analysis. It
Figure 3 Various glow discharge configurations. A) coaxial cathode; B) planar diode; C) hollow cathode lamp; D) Grimm glow discharge; E) hollow cathode plume.
Figure 3 -- continued.
often serves as the light source for atomic absorption or atomic fluorescence studies, as well as emitting the characteristic lines for emission studies of the lamp material. For its use as a light source, the only requirement is that the hollow cathode lamp contains the same material as the atom of interest in the sample to be analyzed. This source operates at lower voltages and higher currents than other glow discharge devices due to the constraint of the plasma within the cathode. This is often referred to as the "hollow cathode effect" [13]. This effect produces a large increase in the intensity of the radiation emitted from the negative glow, making it attractive as an optical emission source. This results in a large increase in the excitation and ionization that is observed in the hollow cathode cavity. This effect has been studied and some theories published [14,15].

**Grimm discharge lamp.** The Grimm glow discharge configuration was first introduced in 1968 [11] and is illustrated in Figure 3D. It is often called an obstructed discharge due to the fact that the cylindrical anode is positioned within one cathode dark space distance from the cathode. The sputtered region of the sample is limited to the region of the cathode enclosed by the anode. This source has found primary use for atomic emission studies. The anodic sampling of this source produces ions with a narrow energy distribution and is well suited to analysis in a quadrupole instrument, which behaves best with ions having narrow energy bands.

**Hollow cathode plume.** This source is shown in Figure 3E. This source was developed by Marcus and Harrison [16] primarily for atomic emission studies.
The hollow cathode plume (HCP) results from the restriction of a hollow cathode discharge to a 1.5 mm orifice in the base of a normal hollow cathode. Samples must be formed in the shape of a disk, with a central orifice, that may be mounted in the base of a graphite cylinder and used as the cathode. These disks may be machined or pressed depending on the nature of the sample. HCP discharges operate at about 1 Torr pressure and currents in the 50 - 200 mA range. The applied potential is typically around 1000 V.

**Fundamental Processes in the Glow Discharge**

The diagram in Figure 4 shows the structure and some of the processes occurring in the analytical glow discharge. The various mechanisms, atomization and excitation/ionization, are shown to occur in very distinct areas of the plasma and its surroundings. The atomization process, known as sputtering, occurs at the surface of the sample when argon ions strike the cathode surface. The excitation and ionization processes are shown in the negative glow region and occur as the result of collisions in this relatively field free area. There is little or no potential gradient that exists in the negative glow region since virtually all of the discharge potential is dropped across the small dark space distance (a few millimeters, a distance that depends on the operating pressure of the plasma). Thus, the potential gradient is large within this dark space distance. The following sections will discuss the fundamental processes in more detail.

**Glow Discharge Sputtering**

Glow discharge sputtering occurs when the discharge gas ions strike the surface of the cathode. When an argon ion strikes the surface it will penetrate a
Figure 4  Illustration of the fundamental processes in the glow discharge plasma.
few atom distances into the lattice sending "shock waves" out in three dimensions around the impact point. Actually, it has been reported that the species striking the surface of the cathode is really a "neutralized ion" [17]. These "neutralized ions" are formed as the ion gets close to the metal surface and is neutralized by a field-emitting electron.

If sufficient energy is transferred by the surface collision (in excess of the target's binding energy), a variety of species will be dislodged from the cathode. The masses of the collision partners and the individual cross sections (which depend on the ion velocity and the electronic structure of the partners) will play a role in the sputtering process [17]. Positive secondary ions are often emitted, but the strong potential gradient in the cathode dark space will cause these ions to return to the surface of the cathode and redeposit. These are the species of interest in the technique of secondary ion mass spectrometry (SIMS), where the ions formed at the surface of the sample are analyzed. Electrons are also emitted in GDMS and they are accelerated away from the cathode by the field gradient and pass into the negative glow region. The emission of electrons from the cathode surface sustains the discharge and allows it to continue running. Thus, the glow discharge is a self-sustaining discharge that requires no external excitation to operate. The third particles that are emitted from the surface are ground state neutral atoms from the cathode material. These atoms are the analytically interesting species that are studied with GDMS and make up the main component of the sputtered particle flux that leaves the cathode surface [18,19]. These species migrate into the negative glow by diffusion, where they may be
subsequently atomized and ionized. It is this distinct production of discrete atoms from a solid medium that gives GDMS its relative freedom from matrix effects. Essentially, the solid is being converted into a "gaseous solution" of sample atoms (the analyte) within the argon discharge gas (the solvent).

The efficiency of sputtering (i.e., the number of cathode atoms removed from the surface per impinging ion) is determined by a parameter called the sputter yield (\( \Upsilon \)) [20]:

\[
\Upsilon = \frac{9.6 \times 10^4 \, W}{M \cdot i^+ \cdot t}
\]

where \( W \) is the weight loss of the cathode (in g) due to the sputtering process, \( M \) is the atomic weight, \( i^+ \) is the ion current (in A), and \( t \) is the total sputtering time (in s). The ion current, \( i^+ \), is related to the total current of the discharge, \( i \), by the following equation:

\[
i^+ = \frac{i}{1 + \Upsilon}
\]

where \( \Upsilon \) is the number of secondary electrons released by one ion. Studies of the experimental factors that influence sputtering have been performed mainly using focussed high energy ion beams similar to those used in SIMS [21]. The sputter yield is mainly dependent upon the incident ion mass, the angle of incidence of the incoming ion, the energy of the incoming ion, and the target material [17,22]. A rigorous theoretical consideration of sputtering and sputter yields has been published [23]. In the next few sections, some of the factors that influence sputtering will be discussed.
Incident ion mass

The incident ions that are encountered in glow discharge sputtering are most frequently those from noble gases. Noble gases are used in GDMS because their relatively inert nature will minimize any interactions with the cathode material and they have the ability to provide a good sputter yield since they behave like hard spheres in the "billiard ball-type" collisions. Bay et al. [24] have published a theory to explain the dependence of a sample’s sputter yield on the mass of the ions that are bombarding the sample. The maximum sputter yield of a given target material is proportional to an energy transfer factor, \( \gamma \), which may be determined as follows:

\[
\gamma = \frac{4M_1 M_2}{(M_1 + M_2)^2}
\]

where \( M_1 \) and \( M_2 \) are the masses of the incident ion and the target atom, respectively. It can be seen that the maximum energy transfer will occur when \( M_1 = M_2 \), and the highest sputter yield should be obtained. For this reason argon has been found to be the best choice for sputtering most medium weight atomic elements [22,25]. Sputter yields have been measured using a variety of noble gases by Wehner et al. and were shown to have a periodic trend with the best sputter yields obtained with the noble metals Cu, Ag, and Au [17]. Zinc and cadmium have still higher yields due to their low heat of sublimation but that makes these elements undesirable to have in a high vacuum system [17]. Typical sputter yields obtained using 400 eV Ar\(^+\) for a variety of target materials are
shown in Figure 5 [26,27]. As the mass of the incoming ions is increased, greater sputter yields are obtained for heavier target elements.

**Incident ion angle of collision**

Oechsner [28] has reported a large quantity of data concerning the influence that the angle of incidence has on the sputtering yields. At angles of 60 - 70° from the normal, it was found that sputter yields (in the energy range from 0.5 - 2 keV) rise to maximum values which are 1.5 - 2.4 times higher than that obtained for normal incidence ions (see Figure 6). The sputter yield showed increases in this range for metals that normally would produce low sputter yields [17]. In these ion beam studies, it was determined that the ion current density decreases with the cosine of the angle \( \alpha \) between the beam and the surface normal. Thus, if there is a sputtering rate increase, it is much less than the yield increase. The dotted line in Figure 6 shows the reciprocal of the \( \cos \alpha \) dependence of \( Y(\alpha)/Y(0) \). Above this curve is the region where a higher sputter removal rate is achieved with an ion beam. However, unless the surface is rotated or sputtered from different angles, it is most often best to sputter with incoming ions normal to the sample to alleviate problems that occur with surface roughening [17].

**Incident ion energy**

Wehner has performed experiments using a high vacuum beam to determine that the minimum kinetic energy that is required to dislodge an atom from its matrix is approximately four times the heat of sublimation of the material [17,29]. For argon, the threshold for sputtering ranges from 13 eV for aluminum
Figure 5: Sputter yield of multiple elements under 400 eV argon ion bombardment [26,27].
Figure 6  Sputter yield increase of Cu with bombardment of various noble gas ions under oblique incidence. The dashed line is the $1/\cos \alpha$ curve, separating rate increase from rate decrease. [28]
to 33 eV for tungsten. Once this threshold is surpassed, the sputter yield will increase rapidly with increasing ion energy, reach a plateau, and then decrease as the energy continues to rise. This plateau region generally occurs with about 1 keV ion energy, but will vary slightly with the discharge gas and the sample. The yields for some elements under different conditions are shown in Table I. These values will show some scatter because the sample may have different surface roughness, a preferred crystalline orientation within a nominally polycrystalline sample, or the possible buildup of impurity layers on the target during sputtering [17].

As previously mentioned, when an ion hits the sample surface it becomes imbedded in the matrix and its kinetic energy is absorbed by the atoms in the vicinity. At lower ion energies the penetration is limited to the surface of the sample where the atoms are disturbed and ejected from the matrix. However, at higher energies the penetration depth of the ion increases, which results in damage to the sample matrix at a distance too far from the surface to affect these atoms. Thus the sputter yield will decrease at these higher energies [17].

In the glow discharge, the energy of the incoming ion is not easily determined because of the energy losses caused by the collisions that the incoming ion encounters as it passes through the discharge dark space. Attempts to determine this energy in the glow discharge have been addressed [30,31]. Calculations (based on the pressure and cathode fall potential of the discharge) have been performed to determine the average energy of the incoming ions hitting the cathode under typical discharge conditions [25]. An ion energy
TABLE I. Sputtering Yields in Atoms/Ion for Some Elements Under Different Argon Ion Bombardment Energies

<table>
<thead>
<tr>
<th>Element</th>
<th>500 eV</th>
<th>1 keV</th>
<th>10 keV</th>
</tr>
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<tr>
<td>C</td>
<td>0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.5</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>0.5</td>
<td></td>
<td>2.1</td>
</tr>
<tr>
<td>Cr</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>1.1</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>1.45</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>2.4</td>
<td>3.6</td>
<td>6.6</td>
</tr>
<tr>
<td>Mo</td>
<td>0.8</td>
<td>1.1</td>
<td>2.2</td>
</tr>
<tr>
<td>Ag</td>
<td>3.1</td>
<td>3.8</td>
<td>8.8</td>
</tr>
<tr>
<td>Au</td>
<td>2.4</td>
<td>3.6</td>
<td>8.4</td>
</tr>
</tbody>
</table>

Source: Reference [17].
range of 100 eV - 575 eV, corresponding to an applied voltage range from 400 - 2000 V dc, was found to be the typical value for the bombarding ions.

**Target material**

The dependence of sputter yield versus target material was shown in Figure 5, where different elements under identical ion bombardment conditions showed periodic trends in their sputter yield. The sputter yield will increase within any one period of the periodic table. These differing sputter yields may become a problem when analyzing alloys or other materials that contain many elements and is called preferential sputtering [32,33]. It was found that preferential sputtering will cause the surface composition of the sample to change and be enriched by the species with the lower sputter yield. The initial consequences of this process is a difficulty in obtaining an atom population in the gas phase that is proportional to the concentrations of the species in the bulk sample. However, the processes inherent to the glow discharge will passively correct for this difference, because the cathode surface enrichment of the lower sputter yield species will lead to an eventual equilibrium state [34]. Thus, after the initial sputtering time required to establish this equilibrium has passed, the gas phase atom population will be proportional to that of the bulk sample.

**Glow Discharge Excitation and Ionization**

Aside from being an efficient source of atom generation, the glow discharge will also excite and/or ionize the sputtered sample atoms through a variety of energy transfer processes. These processes occur primarily in the negative glow region, because the negative glow region is an environment rich
in collisions that may result in the ionization of the sample atoms. Kinetic and/or potential energy may be transferred by a collision partner that is sufficient to excite electrons of the target species to higher energy states [35]. In some cases the electron may be removed completely. It was determined by Harrison and Loving that ionization is occurring throughout the volume of the plasma, but only the ionization that takes place directly adjacent to the exit orifice will be observed by the mass spectrometer [36]. This is because an ion that is formed in other regions of the plasma will undergo further collisions on its way through the source and would never make it to the ion exit orifice.

There are three primary types of collisions that are occurring in the negative glow region of the discharge. They are collisions involving discharge electrons, collisions involving excited discharge species, and collisions involving discharge ions. These collisions will lead to excitation, ionization, and some recombination of discharge species. Table II lists some of the most important ionization mechanisms that occur in the negative glow region. The two mechanisms that are thought to provide a major contribution to the overall ionization of sputtered species in the plasma are electron ionization (El):

\[ M^o + e^- \rightarrow M^+ + 2e^- \]  

where \( M^o \) is a neutral analyte atom, \( e^- \) is an electron, and \( M^+ \) is an analyte ion, and Penning ionization (PI):

\[ M^o + Ar^* \rightarrow M^+ + Ar^o + e^- \]  

(5)
<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>I) Electron Ionization</td>
<td>$M^o + e^- \rightarrow M^+ + 2e^-$</td>
</tr>
<tr>
<td>II) Penning Ionization</td>
<td>$M^o + Ar^* \rightarrow M^+ + Ar^o + e^-$</td>
</tr>
<tr>
<td>III) Associative Ionization (Homonuclear)</td>
<td>$Ar^* + Ar^o \rightarrow Ar_{2}^+ + e^-$</td>
</tr>
<tr>
<td>IV) Associative Ionization (Heteronuclear)</td>
<td>$M^o + Ar^* \rightarrow ArM^+ + e^-$</td>
</tr>
<tr>
<td>V) Nonsymmetric Charge Transfer</td>
<td>$Ar^+ + M^o \rightarrow M^+ + Ar^o$</td>
</tr>
<tr>
<td>VI) Symmetric (Resonance) Charge Transfer</td>
<td>$Ar^+<em>{(fast)} + Ar^o</em>{(slow)} \rightarrow Ar^o_{(fast)} + Ar^+_{(slow)}$</td>
</tr>
<tr>
<td>VII) Dissociative Charge Transfer</td>
<td>$Ar^+ + MO \rightarrow M^+ + O + Ar^o$</td>
</tr>
</tbody>
</table>

$M^o =$ neutral analyte atom  
$M^+ =$ analyte ion  
$Ar^* =$ argon metastable atom  
$Ar^o =$ neutral argon atom  
e$^-$ = electron
where $\text{Ar}^*$ is an argon metastable atom and $\text{Ar}^0$ is a neutral argon atom. These modes of ionization will be discussed in the following sections.

**Electron ionization**

Electron ionization (El) in the glow discharge is accomplished through electrons that are accelerated across the cathode fall region or by electrons existing in the discharge that possess energy in excess of the ionization potential of the target atom. This mechanism is an important source of ionization in the glow discharge [37], and is thought to be the primary ionization path for the discharge gaseous species in the plasma [38]. If a collision occurs involving an electron possessing an energy below the ionization potential, but above the lowest excitation potential of the target atom, electronic excitation of the species will occur [39]. If the excited species can radiatively relax, then the transition may be probed by optical spectroscopy. If radiative relaxation is forbidden, the excited state may exist in the plasma for milliseconds before an alternative deexcitation process may occur [40]. These species are referred to as metastable species and they may lead to further excitation and ionization of other species. If an electron possesses little or no kinetic energy, it is subject to recombination collisions with discharge ions. The excess energy may result in the creation of excited neutrals or metastables [41].

The electrons that are present in the glow discharge differ in both their origin and their energy. There are three general classes of electrons based on these differences [37]. First, there are the fast electrons with energies exceeding 25 eV. These have been accelerated away from the cathode across the dark
space. The second class is the electrons that were created by ionizing collisions in the negative glow region. These are referred to as secondary electrons and have an average energy about 7 eV. The final class of electrons is called "ultimate electrons." These are electrons that have been thermalized (with a mean energy less then 1 eV [42]) by collisions with other plasma species.

**Penning ionization**

As mentioned in the previous section, long-lived metastable species may be formed within the glow discharge plasma and be deexcited by collisional relaxation processes. When this occurs, the transfer of energy from the metastable species to the collision partner results in excitation or ionization of the atom. Two such processes are considered to play a major role in glow discharge ionization. These are Penning ionization, [43] which was shown earlier in equation (5), and associative ionization [44], which will be discussed in the next section.

If the internal energy of the metastable atom is greater than the ionization energy of the collision partner, then an electron-ion pair is created. As mentioned previously, this process is believed to be the primary ionization mechanism for sputtered species in the glow discharge. Table III shows some of the energy levels of the noble gas atoms that are used for glow discharge operation. Argon is usually the preferred gas for GDMS because of its metastable internal energies of 11.5 and 11.7 eV. These energy levels are above the first ionization energies of most elements, below the second ionization energies of many elements, and are below the ionization energy of atmospheric contaminants.
TABLE III. Low-lying Metastable Levels of Rare Gas Atoms

<table>
<thead>
<tr>
<th>Gas</th>
<th>Metastable Energy, eV</th>
<th>Ionization Energy, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>19.8, 20.7</td>
<td>24.58</td>
</tr>
<tr>
<td>Ne</td>
<td>16.6, 16.7</td>
<td>21.56</td>
</tr>
<tr>
<td>Ar</td>
<td>11.5, 11.7</td>
<td>15.76</td>
</tr>
<tr>
<td>Kr</td>
<td>9.9, 10.5</td>
<td>14.00</td>
</tr>
<tr>
<td>Xe</td>
<td>8.3, 9.4</td>
<td>12.13</td>
</tr>
</tbody>
</table>

Source: Reference [8].
Other ionization mechanisms

**Associative ionization.**  
Associative ionization, shown in equation (6),

\[ M^0 + Ar^* \rightarrow ArM^+ + e^- \]  

is the mechanism that is responsible for the production of polyatomic species that contain discharge gas atoms (i.e., the argides in an argon discharge) [38]. The mechanism is similar to the Penning process except that the collision partners remain together and form an ion cluster. The electron that is released during the reaction will carry off any excess energy.

**Charge transfer reactions.**  
The charge transfer reactions listed in Table II are of two types [37]: symmetric and asymmetric. Symmetric reactions involve collisions of like partners. These reactions may lead to the formation of fast neutral atoms as an accelerated gas ion collides with a neutral gas atom [37]. It is believed if this happens in the dark space region, sputter enhancement will occur because of an increase in the number of species bombarding the surface. Asymmetric reactions are a potentially important mechanism for the ionization of sputtered species in some glow discharge configurations. Asymmetric reactions are believed to be the principal ionization mechanism for sputtered species in an obstructed discharge [45] and are responsible for the production of excited ions of sputtered material in hollow cathode vapor lasers [46].

**Analytical Considerations for GDMS**

Glow discharge mass spectrometry has found wide application for the analysis of a variety of samples over the past decade, from pure metals and
semiconductors to thin films and ceramics. This section will be used to discuss the considerations that must be made for analytical work with a GDMS system. These considerations are vital for those applications where an accurate concentration value is needed to determine impurities in high purity samples [47] or the abundances of certain critical components, such as in bulk alloys [48] and semiconductors [49].

**Internal Standards**

Internal standards in GDMS employ the matrix element as the internal standard for semi-quantitative analysis. It is assumed that the concentration of the matrix element of a sample is known. In this method, the sensitivity (the ratio of the signal intensity to its concentration) observed for the reference element (e.g., iron in a stainless steel sample) will allow an estimation of the concentration of the analyte using the following equation:

\[
C_{\text{anal}} - I_{\text{anal}} \times \frac{C_{\text{ref}}}{I_{\text{ref}}}
\]

where \( C_{\text{anal}} \) is the unknown concentration of the analyte, \( I_{\text{anal}} \) is the signal intensity of the analyte, \( C_{\text{ref}} \) is the known concentration of the reference element, and \( I_{\text{ref}} \) is the signal intensity of the reference element. These direct comparisons are valid in GDMS since the variation in elemental sensitivities for this technique is on the order of three. In some techniques the sensitivity among the elements varies by orders of magnitude and the direct comparison shown above would not give even semi-quantitative results.
Relative Sensitivity Factor (RSF) Values

For precise quantitative analysis, external standards must be used for GDMS. Two approaches are possible: 1) the use of relative sensitivity factor (RSF) values obtained from standard materials that are similar in content to that of the unknown, and 2) using sets of standards to construct a calibration curve from which the unknown concentration is related to the ion signal intensity.

RSF values were first employed in spark source mass spectrometry (SSMS) and correct for reproducible variations in the observed sensitivities among the elements. These variations can arise from physical, chemical, and instrumental differences. To use RSF values, an element of known concentration must be present in the sample and the analysis conditions used for the unknown and the reference must be the same. The RSF is defined as a ratio of the sensitivity of an analyte element to the sensitivity of the reference element [50]. The concentration of the analyte and the reference must both be known in the standard, while only the reference element concentration needs to be known for the unknown. The RSF value is calculated as follows:

$$RSF = \frac{\left(\frac{I_{\text{anal}}}{I_{\text{ref}}} \cdot \frac{C_{\text{anal}}}{C_{\text{ref}}}\right)}$$

where the components of the equation are the same as for Equation (7) shown for semi-quantitative analysis. The RSF value is then employed as a correction factor for the intensity ratio calculation shown in equation (7). The unknown concentration of the analyte is then calculated as follows:
RSF values have been obtained for a variety of sample types and were determined in this laboratory for stainless steel samples by using an NIST standard reference material 1264A [51]. RSF values in GDMS have also been reported in the literature for a variety of elements [52]. For RSF values to be most accurate, separate RSF values should be calculated for every instrument on which the analysis is to be performed. The calibration curve method has been reported, using a Grimm glow discharge, with the use of seven stainless steel standards [53].

**Instrumentation**

**Mass Spectrometer**

The research presented in this dissertation is centered around the use of a mass spectrometer for fundamental studies of the glow discharge ion source processes. As mentioned earlier, the glow discharge plasma is an efficient atomization source containing processes that may excite and ionize many of the atoms of interest. The mass spectrometer provides an efficient detection system for the ions produced in this source, as well as providing the isotopic information for the elements of interest. The mass spectrometer provides spectra that are simpler and easier to interpret than optical instruments, since each element has specific mass-to-charge ratios for each of its isotopes. Thus the only interference problems occur with different elements having an isotope at the same nominal mass or from polyatomic species that occur at the same nominal mass as an

\[ C_{\text{anal}} = \left( \frac{1}{RSF} \right) \times \left( I_{\text{anal}} \times \frac{C_{\text{ref}}}{I_{\text{ref}}} \right) \]
element of interest. The former problem can be avoided by using an isotope that does not overlap with another element. Almost all elements in the periodic table have at least one isotope with a nominal mass that is apart from any other elemental isotope. The problems of polyatomic interferences are more difficult to solve. Studies have been performed previously using a triple quadrupole mass spectrometer with a glow discharge source to investigate the collision-induced dissociation of some polyatomic species that are present in the plasma [54]. A double quadrupole system has also been reported for sampling an rf powered glow discharge source, with one quadrupole being used as the dissociation chamber [55]. Both of these methods were successful in using low energy collisions with argon target atoms to reduce and/or eliminate species such as $M_2^+$, $MAr^+$, $MO^+$, $Ar_2^+$, and residual gas species.

The experiments for this dissertation were performed on two different mass spectrometers. One of the instruments is based on Extranuclear (now called Extrel) components and is a more research oriented instrument since its source components are readily accessible and easily modified. This instrument was constructed at the University of Virginia and has been described in detail elsewhere [56,57]. This instrument is shown in Figure 7. The second instrument is a prototype mass spectrometer built by Finnigan MAT in Bremen, Germany using Balzers components. This instrument has a more commercial design (i.e., the components are not as easily accessible or modified) and has previously been described [35,51]. A cross section of the Finnigan instrument is shown in Figure 8. This instrumentation section of the dissertation will be used to compare
Figure 7. Glow discharge mass spectrometer, based on Extrel components, built at the University of Virginia.
Figure 8  Glow discharge mass spectrometer, based on Balzers components, constructed by Finnigan MAT (Bremen, Germany).
and contrast these two instrument designs and discuss their unique components as well as any special considerations that must be made for each. This section is not meant to be a complete and detailed outline of each individual instrument, although the primary mass spectrometer components will be discussed, since this generally applies to either instrument as well as any other quadrupole based instrument. The Extrel instrument, being more accessible to changes and modifications, is the instrument where new ideas and new source designs are first attempted. Once successful, the modified instrumentation or experiments may be adapted and performed on the Finnigan. The conversion of an experimental scheme from one instrument to the other gives the researcher an idea of the difficulties that might be encountered when taking a new idea and trying to use a commercial instrument to run the experiments. The aspects of instrument modification and successful adaptation to a more restricted and commercially designed instrument are always of high concern. This is especially a problem that may be experienced in an industrial environment where applications usually require adaptation of an experimental scheme to a commercial instrument.

**Ion source**

One of the most apparent differences between the two instruments is the design of the ion source. On the Extrel instrument the ion source is external to the mass spectrometer chamber and may be isolated by a sliding gate valve that can be opened and closed between the ion source and the analyzer chamber. The position of the gate is shown in Figure 7. When the gate is down, a 1.5" hole is in position between the ion source exit orifice and the skimmer cone of the
instrument. With the gate closed the ion source may be vented to atmosphere while maintaining a high vacuum in the mass spectrometer chamber. The source is usually vented with argon gas when changing the sample being used for experimentation. This alleviates some contamination that may occur if air is allowed into the source. The ion source, which is constructed from a 2 3/4" six-way cross (MDC Vacuum, Hayward, CA), is larger in volume than the Finnigan source.

The Finnigan instrument has its ion source mounted on a stainless steel tube and inserted into a position within the first pumping chamber of the mass spectrometer. The Finnigan ion source is constructed from a 1" Cajon ultra-torr tee and its position in the instrument is shown in Figure 8. This source cannot be vented to atmosphere without venting the entire mass spectrometer. Thus a sample introduction assembly was constructed [51] to allow the sample to be changed without venting the instrument. This assembly is shown in Figure 9. The principal components of this assembly are labeled in the figure. The ion source is attached to a stainless steel tube that is welded to a vacuum flange and attached to the instrument through an adjustable bellows. The positioning of the discharge chamber in three dimensions is controlled by three turnbuckle screws located 120° apart around the bellows. This allows the ion exit orifice of the discharge chamber to be aligned coaxially with the skimmer cone orifice, as well as allowing the distance between the two to be adjusted. The ball valve in the assembly allows the mass spectrometer to maintain its vacuum after removing the direct insertion probe. While the probe is in place, a 1/2" Cajon connector seals
Figure 9  Glow discharge mass spectrometer sample introduction assembly for the Finnigan instrument.
around the probe with an O-ring allowing the vacuum to be maintained. A roughing pump is required to pump air out of the small volume between the Cajon connector and ball valve when a new sample is inserted. Otherwise, the short burst of air will cause a high pressure condition in the instrument, causing the protection circuit to shut off the pumping system to protect the turbomolecular pumps. During normal operation the roughing pump is isolated from the system. The design of the direct insertion probes used in these experiments has been described elsewhere [51]. The probes are identical for both instruments other than their length. A different probe was constructed for the electrothermal introduction of solution samples and will be described in Chapter 2.

Einzel lenses and Bessel box

The einzel lenses are constructed from stainless steel tubes and are used to direct the ions formed in the source into the mass spectrometer. These lenses are only used for the transport of ions and are only present on the Extrel instrument in this laboratory. Einzel lenses are required in this system due to the relatively long distance from the ion exit orifice to the skimmer cone. This distance cannot be minimized because the Extrel instrument includes the gating valve to isolate the source from the mass analyzer. These lenses are not shown in Figure 7 but are contained within the arm of the six-way cross between the ion exit orifice and the mass spectrometer skimmer cone. The einzel lens system is shown in the left half of Figure 10. The lenses are powered by a 1000 volt power supply (Hewlett-Packard Model 6521A) that allows all of the lens voltages to be independently adjusted from 0 to -1000 V. Einzel lenses are not required in the
Figure 10: Schematic diagram of the einzel lenses and Bessel box energy discriminator for the Extrel instrument.
Finnigan instrument since the bellows assembly allows the ion exit orifice of the source to be placed very close to the skimmer cone.

After the skimmer cone in both instruments lies a Bessel box energy analyzer, which allows only a small bandwidth of ion energies to pass into the quadrupole mass filter. The construction of a Bessel box is shown in the right half of Figure 10, illustrating the complete lens system for the Extrel instrument. The Bessel box lenses are powered by an Extrel Ionizer Control Model 020-2. The lensing system for the Finnigan is shown in Figure 11 that illustrates the lens layout as well as the position of the quadrupole analyzer. These lenses may each be biased from 0 to +/- 140 V and this value is determined by the control circuit illustrated in the figure.

The principle behind using an energy analyzer is that the quadrupole system will operate most efficiently with ion energies from 0 - 10 eV and the glow discharge source produces ion energies from 0 - 20 eV [57,58]. Also any neutral species and photons that come from the ion source will collide with the center beam stop that is positioned in the middle of the second lens (housing). The Bessel box will allow ions within 1 - 2 eV of the voltage applied to the housing to be passed into the quadrupole; this may be tuned not only to give maximum ion signal to the detector but also to allow "tuning" of the mass spectral peaks to give a Gaussian distribution around the nominal mass number. Ions with a small energy will be repelled back out of the Bessel box by the voltage on the housing. Ions with large energies will collide with the housing or the central beam stop since they are too energetic to be curved through the device. Ions in the correct
Figure 11  Illustration of the ion optics system for the Finnigan instrument.
energy band will be deflected around the central beam stop and then focussed through the exit lenses into the quadrupole mass analyzer.

**Quadrupole mass filter**

The mass separation system for both instruments is based on a quadrupole mass filter. This mass separation technique has widespread use and has been previously described [59]. Mass separation with a quadrupole system is based on the mass-to-charge ratio \((m/z)\) of the various ions produced from the sample. The major difference of the quadrupole systems on the two instruments in this laboratory is the size of the rods that are used. The Extrel system has stainless steel rods that are 220 mm in length and 19 mm in diameter. This provides an internal field radius (the distance from the central axis of the rods to the closest surface of each rod) of 8.22 mm providing a mass range of 1 - 380 amu. The Finnigan instrument has 200 mm long rods with a diameter of 8 mm, resulting in a field radius of 3.45 mm that passes specific masses from 1 - 511 amu. The Finnigan system uses a QMA 150 quadrupole system (Balzers, Liechtenstein). Thus, both systems give a wide enough mass range to pass all of the elemental species of interest (approximately 1 - 250 amu). The basic operating principles of both quadrupole systems are the same and will be described below.

A quadrupole system consists of a set of four stainless steel electrodes, which ideally have a hyperbolic cross section, that are accurately positioned in a radial array. A block diagram of a quadrupole system is shown in Figure 12. Since the construction and mounting of hyperbolic rods is more difficult and
Figure 12  Schematic diagram of a quadrupole mass analyzer.
expensive, many quadrupole systems employ electrodes that have a circular cross section. Denison [60] has previously shown that a good approximation to an ideal hyperbolic field may be obtained if the radius of the electrodes \( r \) is related to the quadrupole field radius \( r_0 \) by the expression,

\[
    r = 1.148 \ r_0
\]  \hspace{1cm} (10)

The filtering mechanism of the mass analyzer is obtained by the simultaneous application of dc and ac signals. This will produce an ion trajectory through the quadrupole that follows a very complicated path with only one specific mass-to-charge ratio being passed at any one time. The operation of the quadrupole system will be explained here in a qualitative manner by considering the physical effects in the X-Z and Y-Z planes separately. The Z axis is defined along the length of the rods, while the X and Y axes pass through the center of the opposite rod pairs (see Figure 12). A positive dc potential is applied to the two rods lying in the X-Z plane, while the rods in the Y-Z plane experience a negative dc potential [61]. The rf potentials applied to the pairs of rods are opposite in polarity to one another and are 180° out of phase.

Here the previously mentioned planes will be considered separately as to the mass-dependent effects of each pair on the trajectories of some ions. First, the trajectories in the X-Z plane will be discussed. If an ion is heavy or the frequency of the rf potential is very high the ion will feel primarily the effect of the average potential applied to the electrode. In this case heavy ions are mostly influenced by the positive dc potential and will be focused onto the center axis of the rods. The times when the dc potential is negative will have a negligible
effect on heavy ions. However if the ion is light the varying rf potential may have a greater affect on its trajectory. If it is sufficiently light it may experience an acceleration during the negative voltage cycle that will cause it to collide with an electrode. By this means ions are filtered according to their mass-to-charge ratio. Thus ions with a mass below a critical m/z value will be filtered out of the beam and ions above the critical m/z will be transmitted through the device to the detector. By increasing the rf voltage, heavier ions can be displaced by the rf field. Thus a high-pass mass filter is formed in the X-Z plane (see Figure 13A).

Second, the effects in the Y-Z plane will be considered. The potential applied to the electrodes in the Y axis is always equal in magnitude and opposite in sign to the potential applied to the electrodes in the X axis. Thus, as mentioned previously, the rf potentials in the X-plane electrodes are 180° out of phase with the potentials in the Y-plane electrodes. Also the dc potential applied to the X-Z plane is positive, while that of the Y-Z plane is negative. As before, heavy ions will be primarily influenced by the average dc potential. However, in the Y-Z plane this potential is negative. This means that the heavy ions will be defocussed away from the central axis of the system and eliminated from the beam. Conversely, the ions that are lighter will respond to the focussing action that occurs when the positive portion of the alternating field becomes larger than the static negative potential. If the frequency and the magnitude of the rf field are well chosen, the rf potential may be considered to correct the trajectories of light ions and prevent them from striking the rods along the y axis. Increasing the rf voltage increases the mass-to-charge ratio that is allowed to pass through the
Figure 13  Mass filtering in the quadrupole. A) X-Z plane, high-pass filter; B) Y-Z plane, low-pass filter; C) combination of both planes, band-pass filter [59].
quadrupole. This brief explanation has been discussed in more detail and some models proposed by Dawson [62]. Thus in the Y-Z plane, the electrodes and applied potential combine to result in a low-pass mass filter (see Figure 13B).

If an ion is to travel through the quadrupole to the detector on the other side, the ion must be stable in both the X-Z and Y-Z planes. Thus an ion must be sufficiently light so as not to be eliminated by the low-pass filter of the Y-Z plane but not so light that it is eliminated by the high-pass filter in the X-Z plane. Thus a band-pass filter is created where a narrow mass range of ions are transported through the quadrupole filter to the detector (see Figure 13C). The mass corresponding to the center of the mutual stability region is governed by the magnitude of the applied ac and dc potentials.

The equations of motion in a quadrupole system can be quite complicated. Therefore, a brief discussion will be presented here and more information may be obtained from the references cited within this section. The motion of the ions in the x and y directions depends on the variation of the potential, $\phi_0$, with time as expressed in the following equation [63],

$$\phi_0 = U - V \cos (\omega t)$$

(11)

where $U$ is the dc voltage, $V$ is one half of the peak-to-peak rf voltage and $\omega$ equals $2\pi f$ with $f$ being the rf frequency. It was determined that for a sinusoidally operated hyperbolic mass filter, the potential distribution ($\phi$) at time ($t$) is then expressed as [59],
\[ \phi = [U + V \cos (\omega t)] \frac{(x^2 - y^2)}{2r_o^2} \] (12)

where \(x\) and \(y\) are the distances along the given coordinate axes, \(r_o\) is the quadrupole field radius. Equation (12) is then differentiated relative to the \(x\) and \(y\) axes to calculate the intensity of the electric field \((E)\) along the \(X-Z\) and \(Y-Z\) planes [59]. The results are as follows:

\[ E_x = -\frac{\delta \phi}{\delta x} = -[U + V \cos (\omega t)] \frac{x}{r_o^2} \] (13)

and

\[ E_y = -\frac{\delta \phi}{\delta y} = [U + V \cos (\omega t)] \frac{y}{r_o^2} \] (14)

These equations can then be mathematically converted to the Mathieu type equations by first considering the equations of the force that an ion feels in each plane and substituting Newton’s law \((F = ma)\) [62]. The final results of these calculations are shown in Equations (15) and (16),

\[ \frac{d^2x}{dt^2} + [U + V \cos (\omega t)] \frac{ex}{mr_o^2} = 0 \] (15)

and

\[ \frac{d^2y}{dt^2} - [U + V \cos (\omega t)] \frac{ey}{mr_o^2} = 0 \] (16)
The solutions to these equations are usually unbounded, which corresponds to the rejection of ions from the mass filter. Stable solutions may be obtained only for certain values of \( m, r_o, f, U, \) and \( V \). These solutions will correspond to conditions that will give a successful transmission of an ion through the quadrupole. The following substitutions (known as the Mathieu parameters) are usually made to allow these equations to be written in a single expression [63].

The Mathieu parameters are:

\[
a = \frac{4eU}{m\omega^2 r_o^2}
\]

(17)

and

\[
q = \frac{2eV}{m\omega^2 r_o^2}
\]

(18)

These substitutions represent the dc voltage counterpart \( (a) \) and the rf voltage amplitude \( (q) \) [59,63]. A typical stability diagram is shown in Figure 14, which is constructed by plotting dc voltages that yield stable solutions vs. rf voltages that yield stable solutions. The area below the triangular region represents the values of dc and rf voltages resulting in a stable ion trajectory for this mass.

To generate a mass spectrum, the alternating voltage, \( V \), is scanned, with the direct voltage, \( U \), following it with a given ratio along a scan line that is anchored at the origin in the diagram. Two different scan lines are shown in Figure 14. The top one will result in more triangular peaks, but will have a lower intensity since the area of stability traversed is small. The lower scan line will increase the signal intensity of the ion but will result in broad trapezoidal peaks.
Figure 14  Mathieu stability diagram for a single mass-to-charge ratio in a quadrupole mass spectrometer. [57]
Each given mass will have a slightly different stability diagram. Figure 15 (modified from reference [63]) shows the stability diagrams for four different masses superimposed on the same diagram with actual voltages on the axes. This diagram may be used to demonstrate the principles of resolution and intensity and how they interrelate. The mass scan line given is one that may typically be used in GDMS where unit mass resolution is required. Note that as the mass scan line passes out of the stable region for mass 28 it just begins to enter the stable region for mass 29. This will give unit resolution. If the slope of the line is decreased, then the mass scan line would intercept more of each ion's stable area (resulting in greater intensity), but for two adjacent ions the mass scan line would pass through portions of their stability region at the same time. Thus, the operator must realize that when using a quadrupole system there are trade offs between good resolution and good signal intensity.

**Ion detection**

Both instruments have dual detection systems. Each has a Faraday cup to detect the matrix species and other large ion signals. For the detection of minor and trace species, the Extrel system utilizes a channeltron continuous dynode electron multiplier (Galileo Electro-Optics Corporation) and the Finnigan uses a discrete dynode electron multiplier (Balzers SEV 217, Liechtenstein). Both of these detectors are set off-axis to the quadrupole axis. These detectors may be operated in an analog mode that detects the small currents hitting the detectors or an ion counting mode that will detect discrete events when single ions strike the detector.
Figure 15  Mathieu stability diagram for several mass-to-charge ratios in a quadrupole mass spectrometer (modified from [63]).
Faraday cup. The Faraday cup is the simplest detector employed in mass spectrometry. It consists of a metal plate (electrode) that is used simply to collect the ions that strike it. The ions are neutralized on the surface of the electrode by a transfer of electrons, and the current that results is equal to the incoming ion current. The Faraday electrode is enclosed, except for a small entrance aperture that allows the incoming ions to pass through. This shielding will prevent secondary electrons from escaping before striking the electrode, which could lead to erroneous readings. The detected currents on the Faraday electrode are usually small and a high gain signal amplifier is needed. The Faraday detector requires a well insulated system in order to reduce any leakage currents. The minimum current that is detectable using this detector is approximately $10^{14}$ amps [63].

Channel (continuous dynode) electron multiplier. Channel electron multipliers (CEMs) are widely used as detector devices in many quadrupole mass spectrometer systems [64]. The characteristics of CEMs that have lead to their widespread use include their excellent signal-to-noise (with dark counts of less than 0.5 counts per second), a stable dynode surface that can be exposed to air without degradation of performance, low power requirements, compact size, and a narrow gain distribution of output pulses. CEMs are constructed from a formulation of glass that is heavily doped with lead. The fabrication produces a glass that exhibits secondary emissive properties and resistive characteristics. The Channeltron detector typically has a resistance of about $10^9$ ohms. Electrical contacts are deposited on both ends of the channel to allow electrical contact of
the CEM to an external high voltage. The external voltage will replenish the charge on the channel wall, as well as accelerate low energy secondary electrons to a level where they will create cascading secondary electrons upon collision with the wall. Gain on the order of $10^8$ is possible. This detector should be operated in a vacuum of at least $10^{-6}$ Torr, since higher pressures will lead to increased background signal and the life of the detector will be shortened.

Ion detection in the CEM is as follows. If a particle has sufficient energy to cause emission of at least one secondary electron upon striking the interior surface of the detector then it may be detected. The secondary electron will be accelerated by the electrostatic field inside the channel until it hits the surface again, which should result in the release of one or more secondary electrons. This cascading process may occur 10 - 20 times in the channel depending on the design of the multiplier. The gain of a CEM does not depend on the length of the channel or the diameter of the channel alone. The gain is a function of the ratio of the channel length to its inner diameter [65] as well as a function of the potential difference from end to end (i.e., the applied high voltage). Using this knowledge, channeltron multipliers have been constructed with very small sizes and in arrays. The detection efficiency of a CEM was found to be a function of the incoming ion energy, its velocity, and the degree of ionization [66].

Discrete dynode electron multiplier. The secondary electron multiplier (SEM) operates in a fashion somewhat similar to the CEM. In the SEM, ions coming from the mass spectrometer are accelerated by an electric field and strike an electrode (or dynode), which is made of a material with a high coefficient of
secondary electron emission. These electrons will in turn produce more secondary electrons that are accelerated by the field to a second dynode where they hit and produce other secondaries. This process repeats until a large number of electrons from the last dynode strike a Faraday plate, which generates a large signal. The current is amplified as mentioned previously in the discussion of the Faraday cup. The first dynode of the detector is usually operated at -1000 to -3000 volts that results in an overall gain of $10^4 - 10^8$. Thus a current of $10^{-18}$ A would be multiplied to about $10^{-12}$ A, which is easily measured by the amplifier. Analog filtering with a bandwidth of a few seconds is usually needed to obtain a good signal-to-noise ratio [63]. The SEM, as well as the CEM, gives improved detection limits and an improved response time over the Faraday cup, which allows the instrument to be scanned faster.

One of the disadvantages with electron multipliers (both CEMs and SEMs) is that the gain will change as the detector ages. This can be corrected by measuring gain curves often and adjusting the operating voltage of the detector. The gain is usually calculated by comparing the voltage detected on an electron multiplier with that on the Faraday cup using the same ion beam. The SEM and CEM can both operate in pulse counting modes, where each individual incident ion produces one pulse. Each single ion that strikes the detector will produce about $10^7$ electrons, which is a readily detectable pulse. The detection limit of the pulse counting mode is determined by the background count rate, which is usually about 1 count per second. Pulse counting circuits are more expensive than are analog measurement circuits; as a result, the ion currents should be
below about $10^{-12}$ A for this method to be worthwhile. Also, if the current is too high, pulse pile-up will occur in the detection system and the counting becomes inaccurate.

**Vacuum system**

The vacuum systems of the two instruments differ, but the requirements and care that must be taken to maintain a vacuum system are virtually the same. The Extrel system uses two diffusion pumps (NRC, Model VHS-4), while the Finnigan uses two turbomolecular pumps (the first chamber is evacuated with a 330 L/s pump and the analyzer chamber is pumped by a 170 L/s pump). One of the difficulties that is encountered when merging a glow discharge system is the pressure difference required to operate the source and the mass analyzer. This problem is alleviated by the use of differential pumping through small apertures between three chambers in the instrument. The ion source operates at a pressure of about 1 Torr while the first chamber maintains a pressure of about $10^4$ Torr. These chambers are separated by a 0.5 mm ion exit orifice. The analyzer chamber is maintained at about $10^6$ Torr during operation and is separated from the first chamber by the small hole in the skimmer cone. The pressure is measured in the ion source of both instruments with thermocouple gauges (Teledyne-Hastings, Model DV-4D).

**Data collection**

Both instruments were operated primarily using a Hewlett-Packard 9816 computer system to control the mass scanning as well as collect the data. A block diagram of the detection and data acquisition system for the Channeltron
detector of the Extrel instrument is shown in Figure 16. The system for the Finnigan is virtually identical in its operation.

For detection in the analog mode the signal is passed through a preamplifier and an electrometer. The signal is then directed to an oscilloscope (Tektronix). The Extrel instrument’s oscilloscope (Tektronix Model 5223 with digitizing time base Model 5B25N) allows real-time mass spectra to be observed since the quadrupole controller operates in conjunction with the oscilloscope to allow an external voltage ramp (from the time base output) to control the mass scan. The analog signal may also be routed through a voltage-to-frequency converter to measure the ion signals on a multichannel analyzer (MCA) (Tracor-Northern TN-7200). Finally, the system is connected to the Hewlett-Packard computer via an IEEE bus system to allow the signal to be converted to a digital signal that may be stored and manipulated with the computer software.

In counting mode, the signal is fed into an amplifier system that will eliminate any signal pulses that are below a given threshold (discriminator feature). The amplification stage provides a high speed source of pulses (30 ns) for signal counting devices. The signal can then be directed to the MCA and collected as counts per channel dwell time. The HP computer may then be used to read the MCA data for subsequent storage, data manipulation, and printing of hard copies with the laser printer.

Neutral Species in the Glow Discharge Plasma

The mass spectrometer system will only allow the study of species that are ionized in the glow discharge ion source. However, it is often advantageous to
Figure 16  Possible modes for ion signal detection with an electron multiplier detector.
correlate the ion population that is measured with the mass spectrometer to the neutral and excited atomic population that exists in the ion source. This is accomplished by interfacing the techniques of mass spectrometry with atomic absorption (AA) to measure the ground state atomic species, or atomic emission (AE) to measure the excited neutral species. These experiments were performed only on the Extrel system since its six-way cross ion source will allow simultaneous measurements to be made.

Mass spectrometer/atomic absorption system

A block diagram of the MS/AA system is shown in Figure 17. A commercial neon or argon filled hollow cathode lamp (HCL) was focussed down to a diameter of about 3 mm that was directly adjacent to the ion exit orifice. After passing through the negative glow, the beam was focussed into a 0.5 M Ebert monochromator (Jarrell-Ash, Waltham, Massachusetts). The intensity of the light beam was detected by a photomultiplier tube (Hamamatsu R956, Bridgewater, NJ) coupled with a photometer (Model 110, Pacific Instruments, Concord, CA). The HCL was powered at a constant current of 6 - 10 mA and a peak voltage of 300 V by a DC power supply (Hewlett-Packard Model 6525A). The output of the HCL was modulated at 50 - 100 Hz by a mechanical chopper (Scitec Instruments). A reference signal from the chopper was directed to a lock-in amplifier (Model 5301, EG&G/Princeton Applied Research, Princeton, NJ), as was the signal from the photometer. The lock-in will discriminate against any background emission signal that is produced in the negative glow. The output signal from the lock-in amplifier was then directed into a voltage-to-frequency
Figure 17  Block diagram of the glow discharge mass spectrometry/atomic absorption system.
converter to allow the signal to be collected on an MCA. The MCA data can then be read by the HP computer and manipulated or stored. The signal may also be simultaneously monitored on an oscilloscope.

**Mass spectrometer/atomic emission system**

A block diagram of the MS/AE system is shown in Figure 18. The emission experimental setup is basically the same as used for absorption, only much simplified. With AE, there is no need for an HCL, chopper, or lock-in amplifier. The emission signal is collected from the negative glow and focussed into the monochromator with one pair of lenses. The detected signal is then fed directly into the oscilloscope and voltage-to-frequency converter, and subsequently into the MCA. The collected data is then stored and manipulated by the HP computer. This system is much simplified since there is no background subtraction requirement for emission measurements.
Figure 18  Block diagram of the glow discharge mass spectrometry/atomic emission system.
CHAPTER 2
FUNDAMENTAL STUDIES OF SOLUTION SAMPLES IN GLOW DISCHARGE MASS SPECTROMETRY

Introduction

As discussed in the first chapter, glow discharge mass spectrometry has found the majority of its applications in the analysis of solid samples [67,68]. However, this chapter will focus on the introduction of solution samples into a GDMS system. Solution analysis with a glow discharge is an advantageous avenue to explore, since many samples already exist in this form. A scheme has been developed that couples a glow discharge, using its ionization abilities, with an electrothermal vaporization device, which is very efficient for sample atomization. This method will reduce any need to manipulate the solution before glow discharge analysis (i.e., mixing with a solid material), although the solvent must be removed prior to placing the sample into the mass spectrometer, since the glow discharge is normally operated at a low pressure (1 Torr). This method uses electrothermal vaporization of the solution residue to introduce the analytes into the glow discharge plasma.

The analysis of solution samples is an obviously important facet of chemistry. Many classic analytical methods were developed from the needs for solution sample analysis. One of the fastest growing modern techniques for the analysis of trace elements in solution is the inductively coupled plasma (ICP) [69].
The detection of analytes in an ICP may be performed using atomic absorption (AA), atomic emission (AE), and/or mass spectrometry (MS). ICP-MS uses differential pumping and skimmer cones with small orifices (similar to that described in Chapter 1 for GDMS) to allow the mass spectrometer to operate in the region of $10^{-6}$ to $10^{-8}$ Torr, while the ion source operates at 760 Torr (1 atmosphere). The ICP technique is amenable to the introduction of a large flow of solution, since the samples are introduced through pneumatic nebulizers that remove most of the solvents. Solvent particulates that may enter the source can produce detrimental effects in the plasma, and the properties of the aerosol relative to the analytical performance of the ICP are of great concern. Differences will occur in ICP emission signals depending on whether the incoming aerosol is wet or dry [70]. It was found that the small amount of residual water remaining after the desolvator did not change the plasma conditions. When the dry aerosol was mixed with $\text{H}_2\text{O}/\text{HNO}_3$ droplets, there was a reduction in the ICP emission signal by 43.1 %. Compared to the GDMS source operation, the ICP is able to handle solution samples more easily, due to its higher source operating pressure, larger pumping capacity, and ability to handle large fluxes of material. The argon flow alone into an ICP is in L/min, whereas the glow discharge only can handle a few mL/min to maintain its operating pressure.

This chapter will begin by briefly reviewing some of the modern analytical techniques that are used for the analysis of trace metals in small volume solution samples. The emphasis of this discussion will center on methods using electrothermal vaporization of the analyte, since the glow discharge solution
analysis system was developed using an electrothermal filament for sample atomization. Finally, the experiments performed during the development of this method will be discussed.

**Electrothermal Vaporization**

Electrothermal vaporization (ETV) is an important technique that is used to provide controlled and fast atomization of a sample deposited onto an electrothermal device. This device can take many different forms, such as a filament of graphite furnace. ETV occurs when a sample, is heated to a temperature above the vaporization point of the elements to be analyzed. As a result, neutral and ionic elemental species are released from the electrothermal device. The atomic population produced may be detected and analyzed by a variety of methods, including AE and AA. The atoms may then be subsequently excited (either from the ETV energy itself, or by other external methods) to produce ions that can be detected by ionic emission, ionic absorption, or, as in the present study, quadrupole mass spectrometry. The following sections will give some background and examples of some techniques using ETV.

**Furnace Techniques**

Many solution analysis schemes use a heating device (such as a flame or furnace) to produce excitation of the species to be analyzed. This section will describe some techniques that use a graphite tube furnace in conjunction with a glow discharge hollow cathode plasma to study the atoms and ions from a solution sample. The methods discussed here rely on the glow discharge processes to provide the excitation or ionization, so they are termed "nonthermal
excitation" methods. The ETV/GDMS method that was developed for the solution analysis to be described later was based on some of the principles of these techniques.

**Furnace atomic nonthermal excitation spectroscopy**

The solution sampling method reported in this dissertation is a variation on the furnace atomic nonthermal excitation spectroscopy (FANES) technique [71]. In FANES, a thin layer residue is analyzed after solvent evaporation of the solution sample. The evaporation of the solvent and removal of the analyte from the graphite furnace surface is accomplished by varying degrees of heat generated in the furnace by a high current flow. The analyte is then detected by atomic emission from the graphite tube glow discharge. A block diagram of the FANES source is shown in Figure 19. The analysis procedure is as follows: 1) pipetting the sample at atmospheric pressure, 2) drying the sample at atmospheric pressure, 3) ashing the sample at atmospheric pressure, 4) pumping out the source, 5) filling the source with argon, 6) ignition of the hollow cathode discharge, 7) setting the power supply for atomization, 8) detection of the emission pulse, and 9) cooling the source. Each measurement cycle lasts about one minute and is under microprocessor control. The discharge used for FANES is the hollow cathode type that was discussed in Chapter 1. The FANES technique was first reported by Falk et al., who described a new emission source with independent atomization and excitation processes [71,72]. The source was found to have limits of detection comparable to flameless atomic absorption, while orders of magnitude better than ICP emission. Detection limits of the FANES
Figure 19  Schematic diagram of a furnace nonthermal excitation spectroscopy (FANES) source.
technique, using a 50 \( \mu \text{L} \) sample, were in the range of 0.0007 to 16 \( \mu \text{g/L} \) depending upon the element under study. Also, the FANES method was shown to exhibit a high dynamic range and multi-element capability. This technique has been compared to other atomic spectroscopic methods in a paper by Falk et al. [73]. Similar to FANES, the furnace ionic nonthermal excitation spectroscopy (FINES) technique has been used to measure the emission from ions that are produced in the source described above. Since this method is also considered nonthermal, the ions are produced from energy provided by the glow discharge plasma in the source.

**Molecular nonthermal excitation spectroscopy**

The technique of molecular nonthermal excitation spectroscopy (MONES) was developed for the studies of molecules in the FANES source. This method has been used for the determination of negative ions that combine with metallic species. For instance, the halides \( \text{F}^- \) and \( \text{Cl}^- \) have been determined by the nonthermal excitation of \( \text{MgF} \) and \( \text{MgCl} \) molecules [74]. For this determination, the glow discharge was formed within a graphite tube operated at 2000 \( ^\circ \text{C} \). The solution containing the halide is mixed with a solution containing the \( \text{Mg}^{2+} \) ions as an additive, with a concentration higher than the halide to promote reaction to form the \( \text{MgX} \) molecule. Upon formation of the \( \text{MgX} \) in the gas phase, molecular absorption measurements were made and detection limits of 0.5 ng of fluorine and 0.24 ng of chloride were obtained. This method shows how reactions may be carried out and studied in an electrothermal device. MONES experiments were developed after preliminary FANES studies indicated the formation of free
atoms and small molecules in these discharges [74,75,76]. Recently a microwave induced plasma has been coupled with the MONES method [77]. In these experiments, nitrogen and oxygen were determined in gaseous and aqueous samples through the formation and emission of NH and OH radicals.

Introduction of Micro-Samples into an ICP

As pointed out in the introduction, ICP methods have provided a means for analyzing solution samples that are introduced into the torch in vast quantities with a large supporting gas flow. The ability of the ICP to desolvate a solution sample and submit ions to the mass spectrometer makes it a very prominent technique for bulk liquid analysis. However, if the amount of solution to be analyzed is in short supply and only a small quantity is available, a conventional ICP cannot be used.

Recently, interest has grown in measuring microliter samples with the ICP by interfacing it with an electrothermal source. This was performed by attaching an ETV device to the ICP torch using 1 - 2 feet of plastic tubing. The ICP argon gas is passed through the graphite furnace as the sample is vaporized, producing an atomic population that is representative of the sample. These atoms are then swept, by the gas flow, into the ICP torch for subsequent ionization. The ICP may be operated in single ion monitoring mode to obtain the maximum sensitivity for a given element or in mass scanning mode to provide multi-element analysis. The advantages of coupling ETV and ICP-MS include detecting elemental sample amounts in the low femtogram (fg) region, performing trace analysis on very small volume samples (µg or µL), and alleviating the matrix and solvent interferences
that may be encountered with a typical ICP-MS analysis. Sensitivity values from 20 - 80 counts/fg have been reported, resulting in detection limits in the low fg range [78]. The measurement precision is in the range of 5 - 20 %. Calibration curves have been found to be linear over 2 - 3 orders of magnitude, although quantitation usually requires using the standard additions method for analysis. Memory effects and matrix influences are considered serious constraints for the ETV-ICP/MS technique and these problems are under investigation.

Solution Samples in the Glow Discharge

Introduction

As previously mentioned, the most common samples analyzed in GDMS are solid materials in the form of pins machined from bulk solids or disks formed in a die using powdered samples. The research presented in this chapter is on the development of a method to introduce small volume aqueous solution samples into the GDMS ion source to broaden its range of application. Since the glow discharge source requires operation in a low pressure environment, it is not amenable to the introduction of solvents in a sample. If a solution sample is introduced into the discharge plasma without desolvation, it may extinguish the negative glow. Therefore, strict control is needed to limit the amount of solvent that is brought into the source. Some methods have been employed over the years in an attempt to provide GDMS solution analysis and reduce solvent effects in the vacuum system. The methods employed generally require placing the sample onto a metal substrate and evaporating the solvent, leaving a thin film of solution residue (containing the analyte atoms of interest) on the cathode surface.
Methods that were performed earlier in this laboratory involved the use of a copper rf hollow cathode source for solution analysis [79], as well as applying a solution to a cupped cathode [80]. In these experiments, the applied sample was evaporated, and then atomized and ionized by the discharge processes. This allowed for analysis of the solution residue by sputter atomization into the glow discharge.

**Electrothermal Vaporization/Glow Discharge Techniques**

When combining electrothermal vaporization and glow discharge ionization, the strengths of both systems may be used. The electrothermal source provides a high current that will sufficiently atomize the solution residue in a short time, while the glow discharge is a very efficient source for excitation and ionization because of the energetic plasma processes. The glow discharge can be used by itself to sputter atomize the sample, but this process is limited by the lower currents allowed in the discharge. Thus, sputter atomization is a slower process that releases the sample over a longer time, reducing sensitivity. For optimum sensitivity, the cathode should be carefully chosen to be nonporous. If the cathode is porous, the solution residue will reside at least partially inside the cathode and will take even longer to analyze. The analyte signal in this case will be constant and long lived, but the detection limits will be reduced. An alternative method has been investigated where the solution was mixed with a conducting powder, dried, and then pressed into a discharge cathode for subsequent analysis [81]. The method is thought to be a step forward in the construction of specific standard cathodes to be used for quantitative glow discharge analysis.
with relative sensitivity factors, since solid standards containing the elements of interest are sometimes hard to find.

Electrothermal vaporization/glow discharge atomic emission

Electrothermal vaporization into a glow discharge (GD) emission source has been demonstrated, using a tungsten wire for atomization of solution samples [82]. In these experiments, silver and boron solutions were studied using atomic emission. The discharge was operated at a current of 60 mA and at 1.2 Torr argon pressure. The maximum filament current of 16 A was used for sample vaporization. The effect of various solution additives on the emission signal was also studied and the presence of up to 1000 ppm of aluminum, calcium, magnesium or sodium had little or no effect when added to a silver solution.

Electrothermal vaporization/glow discharge mass spectrometry

In ETV/GD analysis, the heating of the filament serves as the primary atomization step. Although some atomization will still occur by glow discharge sputtering, the amount of sample loss by sputtering will depend on the temperature of the filament and the time required for the solution residue to be removed by thermal methods. The glow discharge provides the only apparent mechanisms for ionization for the analyte under investigation, but the lack of ionic detection in the absence of a glow discharge is not conclusive evidence that ions are not being formed directly from the energy provided by the filament. The ions formed, if any, may be of the wrong energy to pass successfully through the ion lenses of the mass spectrometer and make it to the detector. One disadvantage of the ETV method is the need to devise detection schemes that will accurately
handle transient signals. The signal peak that is produced from a small volume solution sample will typically last only a few seconds, thus fast detection systems are needed.

The schematic diagram shown in Figure 20 shows a simplified overview of the plasma and its processes for ETV/GD analysis. The analyte to be studied (Zn in this case) is shown to reside on the surface of the cathode (the tungsten filament). The plasma sputtering process will liberate both tungsten and zinc atoms from the surface as the argon ions bombard the filament. This results in some loss of analyte before initiation of the filament current, but the discharge "on" time will be minimized in the sampling scheme, as described later. As with a normal glow discharge, Penning and electron ionization will occur with both the solution residue and filament material atoms.

The results presented in this chapter are intended to show the usefulness of this method for introduction of solutions into the glow discharge. Most of the experimental data are concerned with the fundamental processes that occur in the glow discharge and demonstrate how different characteristics of the discharge environment (such as pressure, voltage, and current) may affect the ion signal and change the analytical usefulness of the method. Also, the presence of a filament carrying current in the vicinity of the glow discharge may show some positive or negative effects on the ion transmission and the signal detected by the mass spectrometer.

This ETV/GD method is of interest as well since it provides a separation of the atomization and ionization steps in the analysis. Experiments that separate
Figure 20  Simplified diagram of the glow discharge processes occurring in the ETV/GD system.
atomization and ionization are always of interest since this provides another dimension with which to evaluate the fundamental processes of the glow discharge. Other experiments have been performed to show the utility of separating atomization and ionization steps in the glow discharge analysis. It has been shown that laser ablation can provide a means of atomizing the sample into a discharge plasma, which subsequently provides the ionization mechanism [83]. These studies show that the atomization and ionization processes are both controlled by the laser and discharge parameters. In parallel, the primary atomization may be thought to occur upon heating the filament, while the primary ionization is provided by the glow discharge.

**Ion Source Development**

**Experiments in a Six-Way Cross**

The initial studies were performed using the Extrel ion source (six-way cross) that was described in Chapter 1. A diagram of this source, with the ETV device in place is shown in Figure 21. The source allows easy access to all of the components inside and application of the solution sample to the filament. A dual high voltage feedthrough, mounted in a 2.75" rotating flange (MDC High Vacuum Products Corp.; Hayward, CA), was used to hold the filament and its supporting assembly. This allowed for ease in filament alignment and replacement. The filament loops for these experiments were 4 mm in diameter and 2.75 mm long and were constructed by coiling a rhenium ribbon 3 turns around a 3.2 mm metal rod. The filament was held in place by two stainless steel rods and a small copper support wire in such a manner that the center of the coil...
Figure 21 Diagram of the ETV/GD ion source used for the initial experimentation.
was aligned coaxially with the exit orifice. This was done because the majority of the solution residue will lie on the inside of the filament loop and ions traveling out from the center of the coil will most likely be directed through the ends of the coil and toward the exit orifice. Set screws secured the support rods to the dual feedthrough as well as mount the filament in a fixed position. Glass shields were constructed to protect the stainless steel rods from the discharge environment, allowing only the filament loop and about 10 mm of a copper support wire to be unprotected. The external cathode was mounted on the end of a probe and placed in the mass spectrometer through a bellows assembly that allowed for placement of the cathode in a variety of positions around the filament coil. The discharge was operated in both constant current and constant voltage mode using a Heinzinger HNCs 2500-150 ump. power supply, allowing operation up to a maximum of 2500 V or 150 mA. The studies discussed here were performed at about 1 mA current and voltages ranging from 400 - 800 V, with pressures in the range of 0.45 - 2.5 Torr. The current loop was powered by a MAT 261 filament power supply (Finnigan MAT; Bremen, Germany), which allows up to 10 A of current to be supplied to the filament for sample atomization. The maximum current varied from 4 - 6.6 amps, depending on the filament material and the analyte to be studied. Table IV shows some materials that were initially studied in order to find an appropriate filament to provide a "white hot" glow capable of vaporizing the analyte of interest. The filament power supply was insulated since it floats at a high potential when the filament was used as the discharge cathode. A stepper motor assembly was constructed to control accurately the output
## TABLE IV. Properties of Some Possible Filament Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Diameter (mm)</th>
<th>Maximum Current (A)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.25</td>
<td>4</td>
<td>glows &amp; melts</td>
</tr>
<tr>
<td>Brass</td>
<td>1.2</td>
<td>6.6</td>
<td>- - -</td>
</tr>
<tr>
<td>Chromel</td>
<td>0.35</td>
<td>2.6</td>
<td>red glow</td>
</tr>
<tr>
<td>Cu</td>
<td>0.9</td>
<td>6.6</td>
<td>- - -</td>
</tr>
<tr>
<td>Ni</td>
<td>1</td>
<td>6.5</td>
<td>- - -</td>
</tr>
<tr>
<td>Re (ribbon)</td>
<td>0.1 x 0.75</td>
<td>4.2</td>
<td>white glow</td>
</tr>
<tr>
<td>Ta</td>
<td>0.015</td>
<td>4.5</td>
<td>white glow</td>
</tr>
<tr>
<td>W</td>
<td>0.010</td>
<td>5.5</td>
<td>white glow</td>
</tr>
</tbody>
</table>
current of the MAT 261. The current was supplied to the filament by RG-59 coaxial cable and high vacuum feedthroughs.

**Filament on a Probe**

A problem with this type of source is that there may be slight differences in the construction of individual filament coils. Also with the rigid support system there is no way to optimize the distance from the cathode to the exit orifice, which is an important parameter for detecting the maximum ion signal with GDMS. Figure 22 shows how the ion signal of tungsten, sputtered from the coiled electrothermal filament, varies with the cathode-to-exit orifice distance. It can be seen that the maximum ion signal occurs when the cathode is about 7 mm away from the ion exit orifice, a typical value for a 1 Torr glow discharge. With these problems at hand, it was realized that a direct insertion probe (DIP) should be used in an effort to solve the problem of positioning. A 0.5" outer diameter DIP, shown in Figure 23, with a 10-turn tungsten filament was constructed to allow the introduction of a solution residue sample into the ion source without venting and with the ability to position accurately the filament coil with respect to the ion exit orifice. The DIP also will allow the use of an auxiliary cathode, if so desired, since the probe contains four vacuum feedthroughs. Two of the feedthroughs carry the electrothermal current and discharge voltage for the filament, while one may carry voltage for an auxiliary discharge cathode. Initial experiments using the DIP show comparable results to those obtained in the six-way cross, although the ion signal can be maximized with the DIP due to its flexibility.
Figure 22  Effects of the cathode-to-ion exit orifice distance on the ion signal obtained from a sputtered tungsten filament coil.
Figure 23: Diagram of the ETV/GD filament cathode mounted on a direct insertion probe.
Experimental

Sample Preparation

Solutions were prepared by mixing an appropriate amount of a metal nitrate with distilled water to obtain the desired cation concentration. The chemicals that were used are as follows: nickel nitrate \(\text{Ni(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}\) (Mallinckrodt Inc.; Paris, Kentucky; Analytical Reagent Grade), zinc nitrate \(\text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}\) (Fisher Scientific; Fair Lawn, NJ; Certified A.C.S.), cupric nitrate \(\text{Cu(NO}_3\text{)}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}\) (Fisher Scientific; Fair Lawn, NJ; Certified A.C.S.), ferric nitrate \(\text{Fe(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O}\) (Mallinckrodt Inc.; Paris, Kentucky; Analytical Reagent Grade), and silver nitrate \(\text{AgNO}_3\) (Mallinckrodt Inc.; Paris, Kentucky; Analytical Reagent Grade). Enough concentrated nitric acid (Fisher Scientific; Fair Lawn, NJ; Reagent A.C.S. grade) was added to the solutions to provide an acidic concentration of 1 - 2 % HNO\(_3\). Fundamental studies of the source properties were carried out with analyte concentrations of approximately 1000 ppm.

Sampling Sequence

The sampling sequence that was devised for the electrothermal introduction of solution samples went through a variety of stages in its development. There were a few considerations to make in order to ensure the most accurate analysis of the samples. First, the solvent on the filament had to be completely evaporated to minimize any detrimental effects that may be obtained by excess water being introduced into the mass spectrometer. Second, the current used for solvent evaporation had to be less than that required to remove the analyte from the filament. Third, the filament material should be
stable for the evaporation step. Some of the filament materials could not withstand the lower evaporation currents when carried out in an air atmosphere. This was particularly true for the rhenium ribbon, which would completely oxidize and break unless the evaporation was performed at a low pressure (≈ 20 Torr) or in an inert gas atmosphere. Finally, the discharge operation time before the filament current is initiated should be long enough to ensure a stable discharge, but as short as possible to minimize any loss of sample analyte due to sputtering.

The final version of the sampling sequence that was used for sample introduction on the DIP is as follows: After bringing the source up to atmospheric pressure, the solution samples (ranging from 10 - 40 μL) were directly pipetted onto the filament loop by a microliter pipet [Volac Model # R 880/A, 5 - 50 μL adjustable volume; Great Britain]. The solutions were evaporated at about 1.5 A filament current for 2 min. The current was increased to 2 A, and the evaporation step continued another 2 min (after this time the coil surface appeared to be dry). The probe was placed into the instrument and the roughing pump applied for 1 min. The sample was allowed to sit under high vacuum conditions for 2 min after placing it into the ion source. The argon was then introduced at the working pressure, usually 1 Torr, and the pressure was allowed to equilibrate for 1 min. The detector was then turned on for 30 s. The MCA was turned on for 5 s to measure any background signal that may be present. The discharge was turned on and allowed to run for 5 s. The filament current supply was turned on to the appropriate atomization current for the sample. After data collection, the filament was allowed to continue heating for 2 min to drive off any remaining species and
reduce memory effects. The filament assembly was allowed to cool for about 5 min before another cycle was repeated with the next sample.

**Data Acquisition**

When studying solution samples with the electrothermal source, the data obtained consisted of a transient signal lasting a few seconds. A schematic representation of the data acquisition scheme is shown in Figure 24. The quadrupole was set to pass the mass of interest and the signal from the detector was monitored using the MCA. The MCA was first turned on to allow detection of any background signal. The discharge was turned on, at \( t = 0 \) s in the figure, for 5 s to allow stabilization of the discharge voltage. This time was chosen as the shortest time to allow a pre-sputtered filament coil to attain a stable discharge. This time was minimized to allow most atomization to take place due to the electrothermal vaporization. The filament was then turned on, at \( t = 5 \) s in the figure, and quickly rises to the desired current. It may be noted that the spikes that are produced at this time are due to electrical noise in the system upon initiation of the filament current. After about a 1 s delay, the ion signal from the solution residue is detected as a peak.

**Filament Materials**

The results that were obtained with different filament materials are discussed in this section. The materials under active investigation were rhenium, tantalum, and tungsten. These were the only three filaments that resulted in the "white hot" glow required for vaporization of the samples (see Table IV for the filaments attempted and some observations). The initial study used a rhenium
Figure 24   Diagram of the relationship between the detected ion signal with respect to the operation of the glow discharge and electrothermal filament.
ribbon as the atomization source. Studies were performed two ways: 1) with the filament acting as the discharge cathode for ionization, and 2) with ionization being provided by the discharge supported by an auxiliary cathode (as shown in Figure 21). Both methods produced comparable ion signals for silver solutions, but the latter technique was subsequently adopted because of its simpler design. If the rhenium ribbon is subjected to multiple runs, the glow discharge sputtering process will "eat" through the ribbon and cause a discontinuity in the current loop. Tantalum wires were also tried as an ETV filament but they too degraded very quickly. The majority of the experiments was performed using a tungsten wire. This wire was the most stable of the three in terms of producing sample ion signals and the long term ability to withstand the sputtering processes.

Filament-Plasma Interactions

The glow discharge processes and operation may be disturbed by the operation of the electrothermal device within the ion source region. This section will describe some considerations that must be made when coupling an electrothermal device, carrying a high current, with the glow discharge device. The experiments described in this section were performed to observe the changes in a typical glow discharge signal when applying a current to the electrothermal filament.

Ion Transmission

The first concern when using the static coil experimental setup was the effect that the filament current would have on the transmission of ions from the auxiliary pin cathode. In these experiments, the discharge cathode was separate
from the filament and the cathode pin could be positioned around the filament. Different positions were investigated for the placement of the discharge pin cathode. These included placing the pin behind the filament, such that atoms from the pin must traverse through or around the filament to reach the exit orifice, placing the pin inside the filament and co-axial to the ion exit orifice, causing the negative glow region to be confined in the cylindrical space defined by the coil, and placing the pin beside the filament coil. The ion signal transmission was found to be greatest with the pin beside the filament coil, so this configuration was used. This orientation was also allowed with the direct insertion probe.

**Effects of different filament currents**

Changes may occur in the glow discharge processes when the filament is carrying a relatively high current (three orders of magnitude more than the discharge itself). A glow discharge pin cathode was operated in the constant voltage mode while being positioned beside of the filament. As the filament current was increased from 0 to about 5 A, the discharge current was monitored. The results of this experiment are shown in Figure 25. The glow discharge current is observed to decrease slightly over the range of 0 - 4 A of filament current. After this point the glow discharge current shows a dramatic increase. This may be the result of electron emission from the filament, which may add to the flow of electrons toward the anode and thus increase the measured current of the gaseous conductor.

The next experiments were performed to observe how the filament current would affect the ion signals when the electrothermal filament itself was used as
Figure 25: Effects of the electrothermal filament current on the glow discharge current when the glow discharge is operating at a constant voltage.
the discharge cathode, since this much simpler experimental design was used most often. The effect of filament current on the Re\(^+\) signal is shown in Figure 26. The reported signal is the peak height of the \(^{187}\)Re\(^+\) isotope after scanning a mass range containing the rhenium isotopes 25 times. The initiation of the filament current results in a fairly constant decline of the ion signal, when operating with a 1 mA constant current discharge. The discharge voltage changes from 598 V with no filament current to 740 V with 3 A filament current. Overall, there is about a 67% decrease in the ion signal from 0 - 3 A, probably due to changes in ion transport induced by the current present near the plasma, possibly as a result of an induced magnetic or electrical field in the area.

These changes were also observed when running the discharge at a constant voltage of 500 V. Figure 27 shows the ion signals for some gaseous species (H\(_2\)O at m/z = 18, COH and N\(_2\)H at m/z = 29, and ArH at m/z = 41) and one sputtered species (Re at m/z = 187) with increasing filament current. All of the ions in this experiment respond in a similar manner and seem to follow the same trend as the discharge current (as seen in Figure 25). Thus, it appears that the filament current (and the subsequent changes in the discharge current) has a major effect on the magnitude of the ion signals obtained from the discharge. This observed increase at the higher current led to subsequent operation of the discharge in the constant voltage mode for the analysis of solutions, since high currents will most likely be used and this will result in a higher ion signal. However, analyte signals from solutions may respond differently depending on their atomization temperature.
Figure 26. Effects of the electrothermal filament current on the $^{187}$Re ion signal obtained from a rhenium filament when the glow discharge is operating at a constant current.
Figure 27  Effects of the ETV filament current on various ion signals obtained from a rhenium filament when the glow discharge is operating at a constant voltage. A) $\Delta\cdot{}^{18}(\text{H}_2\text{O})^+$; B) $\bullet\cdot{}^{29}(\text{COH})^+$ and $\text{N}_2\text{H}^+$; C) $\blacksquare\cdot{}^{41}(\text{ArH})^+$, D $\blacklozenge\cdot{}^{187}\text{Re}^+$. 
Internal ETV Sample Introduction

The internal ETV setup that was used for the majority of the fundamental solution sample studies for this dissertation is shown in Figure 28. This method is termed "internal" since the vaporization occurs within the discharge plasma, and the negative glow is supported by high voltage applied directly to the filament. This method was chosen as the preferred method to use since it is the most simple with respect to the instrumentation requirements. One of the problems that occurs with internal analysis is that the discharge plasma will erode the filament material over time and may lead to inconsistencies in the atomization temperature obtained for a given filament. This is because the filament current power supply output is limited by the wire resistance. As a filament is used and eroded, the power supply maximum output will decrease.

Effects of Different Filament Currents

A parameter that had to be determined for each individual element was the current required to vaporize sufficiently the analyte. Figure 29 shows the ion signal that was detected for a 1000 ppm iron sample that was subjected to various filament currents. Figure 29A shows that when operating with no filament current the ion signal is very low (about 30 counts per MCA channel), but is long lived. Over the observation period shown (about 200 s) the ion signal is constant. Figure 29B shows the ion signal obtained when the filament is operated at 1 A (turned on at $t = 5$ s). The ion signal starts out high and falls to a plateau value that is higher than observed for operation with no filament current. The initial signal peak is probably due to the initial sputtering of the surface residue and
Figure 28  Diagram of the internal ETV ion source.
Figure 29  Ion signal detected from a 20μL sample of 1000 ppm iron that was collected while using various electrothermal filament currents. A) 0 A; B) 1 A; C) 2 A; D) 3 A.
Figure 29 -- continued.
equilibrium of the discharge plasma. This increase in plateau signal may be due to the slight heating of the filament material. Figure 29C shows the ion signal that is obtained when the filament current is operated at 2 A. Again, there is an initial decrease in ion signal as the filament begins to sputter, but when the filament current is initiated a signal peak is produced. This peak is narrow and lasts approximately 5 s, but produces a higher ion signal. The initiation of the filament current causes a temporary increase in the ion signal as the filament is heated, but the signal then falls to a plateau value that is higher than observed with 0 or 1 A filament current. The filament current was finally operated at 3 A (see Figure 29D). The initiation of a 3 A filament results in a large ion signal peak that is at a much higher intensity than any signal previously observed. The maximum ion signal obtained was about 400,000 counts. Since the ion signal obtained in these experiments was reported as the area under the peak, it can be seen how the sensitivity of the ETV/GD technique is increased by using a filament current that quickly removes the analyte, rather than sputtering the thin film residue to remove the analyte more slowly.

Response to Concentration Changes

A problem with using this method for quantitation is that the absolute counts detected for a given sample may differ as a result of changing the filament as needed. However, the ion signal should be consistent when compared using a known concentration and the same filament. A series of Ag\(^+\) solutions was prepared having concentrations of approximately 1, 10, 100, 250, 500 and 1000 ppm. The results obtained using one filament are shown in Figure 30. The
Figure 30  Effects of the silver concentration on the $^{107}$Ag ion signal.
concentration range shown here is quite small, only three orders of magnitude, but the samples used in the experiments described here are within this range. The plot is linear in the lower concentration range, with some deviations being encountered at the higher sample concentrations. The error bars in the figure are calculated as the relative standard deviation for a series of three separate runs. The inconsistencies that were obtained from run-to-run will be discussed further below.

**Pressure Effects**

The glow discharge will operate in a stable manner in the pressure range from a few tenths of a Torr up to five Torr. The purpose of this experiment was to locate the pressure resulting in the largest ion signal from a given amount of analyte. Figure 31 shows two plots that were obtained using an iron pin (in a typical GDMS configuration) while measuring the ion signal obtained at a variety of pressures. The upper curve was obtained after tuning and optimizing the system at a pressure of 1 Torr, while the bottom curve was tuned at the low end of the experimental range (0.45 Torr). Although the intensities of the ion signals obtained under these different tunings are different, the general trend shows that for a normal sputtered species the maximum ion signal is obtained at 1.2 - 1.3 Torr argon. This trend is comparable to previous studies of glow discharge pressure effects. As the pressure is increased or decreased from its maximum a sharp decline is seen in the ion signal. As pressure decreases, the argon metastable population falls off causing an ion signal decrease. This is because Penning ionization, via argon metastables, is the predominant mechanism for
Figure 31 Effects of ion source pressure on the $^{56}$Fe ion signal intensity from a stainless steel cathode. The instrument was optimized at: A) 1 Torr argon and B) 0.45 Torr argon.
ionization in the glow discharge. As pressure increases, a point is reached where the destructive collision rates of the argon metastables will exceed their creation rate, also causing a decrease in ion signal [84].

The ion signals from a silver sample being vaporized from the filament surface were also collected at a variety of source pressures. Figure 32 shows the plot of the ion signal from a 100 ppm Ag⁺ solution. The ion signal reported was the total counts reaching the detector in a period of 15 s totally encompassing the transient ion signal peak. The maximum operating pressure was determined to lie between 1.0 - 1.2 Torr argon. This is in agreement with that obtained using a normal pin cathode.

**Cathode to Exit Orifice Distance**

As previously mentioned, one of the primary motivations for designing the filament source on the probe is the added flexibility of positioning the filament within the ion source. Figure 22 was presented in an earlier section and shows the typical ion signal response for a sputtered species from a solid cathode as the cathode-to-ion exit orifice distance is changed. On the other hand, Figure 33 shows the ion signals from an electrothermally vaporized species (in this case zinc), as well as from the filament (tungsten) as the cathode-to-exit orifice distance was changed. Dramatic differences in the optimum sampling distance are observed between the pin and filament sources. With the presence of a 4 A filament current and a glow discharge operating at 10 mA the optimum sampling distance has decreased from about 7 mm to approximately 3.5 mm. This may be a result of the changes that are occurring within the plasma. The large flux of
Figure 32  Effects of ion source pressure on the $^{107}$Ag ion signal intensity from a 20μL-100 ppm sample.
Relative Ion Signal

Figure 33  Effects of the cathode-to-ion exit orifice distance on the ion signal from a sputtered species (■-\textsuperscript{186}W\textsuperscript{+}) and an electrothermal species (○-\textsuperscript{64}Zn\textsuperscript{+}) while using a 10 mA constant current discharge and a filament current of 4 A.
electrons from the filament, or possible differences in the energy of the ions formed with this source may contribute to this difference. Consequently, further experiments were performed at this distance to obtain the highest ion signal.

Effects of Sample Positioning on the Filament

One parameter that may cause problems in the ETV/GD technique is where the sample is placed on the filament. Using a 20 \( \mu \)L sample size, the sample could be placed in about four distinct locations on the filament. Figure 34 shows the ion signal obtained in these four positions, where position 1 is the end of the coil farthest from the ion exit orifice, and position 4 is the end closest to the exit orifice. There is a generally linear increase in the ion signal as the position of the sample is changed from one end to the other. Thus, care must be taken in placing the sample in a reproducible position on the coil. If the maximum ion signal is desired, then the sample needs to be placed on the end closest to the ion exit orifice.

Memory Effects of the ETV/GD Technique

Another consideration for ETV analysis is the background signal that will be obtained when the solvent alone is placed on the filament and analyzed by the mass spectrometer. Figure 35A shows the signal obtained for a 20 \( \mu \)L sample of a 1000 ppm silver solution. In the next run, a blank sample (containing only the acidic distilled water) was loaded onto the filament coil and the ion signal obtained is shown in Figure 35B. The total ion signal for the silver sample is about 300 times larger than for the blank.
Figure 34    Effects of the positioning of the sample application on the ion signal. Position 4 is closest to the ion exit orifice.
Silver ion signals with the ETV/GD system to determine the presence of memory effects. A) 20µL sample of 1000 ppm silver solution; B) 20µL of a blank solution.
Effects of Contaminant Gas Introduction

The inconsistency of this method can be attributed mostly to the introduction of contaminant gaseous species (air and water vapor) brought into the ion source with each sample. This may be seen by two different experiments. In the first experiment, samples were run in succession and the ion signal is observed to decrease with each sample (probably due to the cumulative effects of constantly introducing more contaminant species). For a 20 µl sample of 1000 ppm Ni⁺ the following ion signals were obtained for four consecutive runs: 6.16 x 10⁶, 5.61 x 10⁶, 3.20 x 10⁶, and 3.60 x 10⁶. After these four runs, the probe was allowed to remain in the high vacuum of the mass spectrometer for 90 min. The next solution sample produced 6.30 x 10⁶ counts, which is close to the signal obtained for the first run. Subsequent runs again showed a continual decrease in ion signal counts. Similar trends were observed for other elements analyzed by this ETV/GD technique. This is probably due to detrimental effects on the ionization processes in the negative glow, since previous experiments that were performed with ETV/GD atomic emission showed fairly consistent data [82]. Also, the contamination effects may be studied by evaporating the solvent in an argon atmosphere versus an air atmosphere. When the ion source on the Extrel instrument was used, an argon atmosphere was employed. For a 20 µL sample of 100 ppm zinc, ion signals of 3.68 x 10⁵, 3.66 x 10⁵, 3.47 x 10⁵, and 3.21 x 10⁵ counts were obtained. If air were drawn into the cross during solvent evaporation, the following ion signals were obtained: 1.48 x 10⁵, 1.15 x 10⁵, 1.41 x 10⁵, and 1.81 x 10⁵ counts. Thus, it can be seen that this method is very susceptible to
atmospheric conditions in which the evaporation step and sample loading are performed. Chapters 3 and 4 of this dissertation will discuss the effects that water vapor has on the processes of the glow discharge, since this is probably the most detrimental contaminant for these aqueous solution studies.

External ETV Sample Introduction

The external ETV setup is shown in Figure 36. The glow discharge is supported by a pin cathode and the atomization filament is external to the negative glow. The atoms are required to diffuse to the negative glow for ionization when using this method. This setup was developed to see if the changes in the filament due to sputtering were a main cause of the inconsistencies in quantitative analysis. Figure 37 shows a comparison of an analysis of 20 μL samples of 100 ppm Zn obtained with both the internal and the external ETV method. Three things should be pointed out: 1) The sensitivity of the internal ETV is much better. This is most likely due to losses as the atoms diffuse to the negative glow in the external setup. 2) The small ion signal that is apparent during the pre-sputter period is not existent in the external method, since the filament is no longer subjected to sputtering. 3) The relative standard deviations are very similar for both methods over the first four runs of a new filament as shown, although both methods will deteriorate over subsequent runs. The external mode, however, will not produce as large a standard deviation (10 - 15%) as the internal mode (20 - 25%). This is probably due to the more stable filament surface conditions that are anticipated with the external method since the filament is not being sputtered.
Figure 36  Diagram of the external ETV ion source.
Figure 37  Comparison of the ion signals obtained for four consecutive runs when using the internal and the external ETV systems. A) Internal ETV; B) External ETV.
Multi-Element Solution Mixtures

Multi-element samples present challenges for ETV/GD analysis, since the analyte signal is only present for a few seconds. This makes it difficult to observe more than one elemental ion signal with each sample. There are, however, solutions to this problem. An alternative is to run a sample for each element individually, but the results may be inconsistent if there are changes in the filament or discharge conditions between experiments. Two methods for detection of multi-elements in the same sample are the use of a lower atomization current to remove the atoms in a slower manner so that the ion signal will be present for a longer time, and taking advantage of different heats of atomic formation for the elements studied.

Mass Spectral Scanning

In this experiment, the filament current was lower than required for analyte atomization, thus providing a longer ion signal duration. This method is suitable for analysis of elements with similar atomization temperatures that cannot be resolved with different filament currents. This allows for analysis of multi-elements by mass spectral scanning. By doing this, isotopic ratios may be observed as well as any interferences that may be present.

An example using this method is the analysis of an iron-manganese mixture, since both analytes are atomized at a similar temperature. Figure 38 shows the mass spectra (a compilation of 10 scans) for the Fe/Mn sample, accumulated one minute after discharge initiation, with 0, 1, 2 and 3 A. The manganese ion is the dominant species in these spectra and shows a maximum
Figure 38  Mass spectra obtained from an iron/manganese mixture using different currents. A) 0 A; B) 1 A; C) 2 A; D) 3 A.
when 2 A of filament current are used. The decrease in ion signal at 3 A is most likely because the bulk of the analyte was electrothermally vaporized before all 10 scans of the acquisition was completed, resulting in an overall lower ion signal intensity.

This method would benefit from a computer controlled instrument that can quickly scan the mass range multiple times while the ion signal is coming off the filament. The computer system used in this laboratory is far too slow to provide this capability. Thus, multi-elements that are analyzed must be in a very small mass range (about 10 amu) to provide any multiple scanning. To perform these experiments most accurately, a computer system such as those used in liquid chromatography/MS applications is needed. This would allow multi-element analysis with the addition of internal standards, which could lead to more accurate analytical results.

Separation of Multi-Element Species with Filament Current

Since the limitation of mass spectral scanning exists, the multi-element species were attempted by removing the analytes in sequence according to their vaporization temperature. This was done by periodically increasing the filament current, which enabled the sequential removal of the analytes from the element with the lowest vaporization temperature to that with the highest. Table V shows some of the thermal properties of the ions under study and the filament currents used to vaporize them. The data for rhenium are given for comparison. The solution analyzed in this experiment was a binary mixture of 1000 ppm zinc and nickel. Figure 39A shows the data obtained for the zinc analyte with the
TABLE V. Heats of Formation and Filament Currents used for the Elements under Study

<table>
<thead>
<tr>
<th>Element</th>
<th>$\Delta H_i$ (kJ/mole)</th>
<th>Filament Current Used (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>415.5</td>
<td>2.5 - 3.4</td>
</tr>
<tr>
<td>Mn</td>
<td>283.3</td>
<td>2.5 - 3.4</td>
</tr>
<tr>
<td>Zn</td>
<td>130.4</td>
<td>2.0</td>
</tr>
<tr>
<td>Ni</td>
<td>430.1</td>
<td>3.0</td>
</tr>
<tr>
<td>Ag</td>
<td>284.9</td>
<td>3.0</td>
</tr>
<tr>
<td>Re</td>
<td>774</td>
<td>- - -</td>
</tr>
</tbody>
</table>

$\Delta H_i$ is the heat of formation of gaseous atoms from elements in their standard states.

Source: Reference [85].
Detection of zinc and nickel from a binary mixture as the filament current is changed. At $t = 5$ s, the current is turned on at 2 A, while at $t = 50$ s the current was increased to 3 A. A) $^{64}\text{Zn}$ ion signal; B) $^{58}\text{Ni}$ ion signal.
quadrupole set to pass m/z 64. At t = 5 s, the filament was turned on to 2 A and the zinc sample was removed from the filament. At t = 50 s, the current was increased to 3 A. An additional small zinc signal was obtained. Figure 39B shows the same analysis sequence with the quadrupole set to pass the 58 isotope of nickel. The majority of the nickel signal was obtained only after increasing the filament to 3 A. In Figure 40, both species were analyzed using only one sample application. With the quadrupole set at m/z = 64, the filament was turned on (2 A) at t = 5 s. At t = 40 s, the quadrupole was changed to pass m/z 58 and at t = 50 s the current was increased to 3 A to remove the nickel. By using this method of carefully controlling the filament current, multi-element samples may be separated and analyzed with the ETV/GD method.

Conclusions

This chapter has shown that electrothermal vaporization may be used to analyze solution samples in a glow discharge mass spectrometer quickly. The fundamental characteristics of this technique were shown to be similar in most respects to those of typical GDMS systems. The sampling sequence is an important part of the method development, since the dryness of the sample is critical and the timing of the steps needs to be accurate. The method described above probably could be improved if the entire sequence of events was under computer control. The experiments discussed above were timed with a stopwatch for accuracy within about 1 s. The amount of sputtering loss before initiation of the electrothermal filament should be minimized, but the sputtering time should be sufficient to provide a stable discharge. This was obtained in a minimum time
Separation of zinc and nickel from a binary mixture using one sample application. At $t = 5$ s, the $^{64}$Zn atoms are removed with 2 A current and at $t = 50$ s, the $^{68}$Ni atoms are removed with 3 A current.
of 5 s, which does not result in the loss of much ion signal (less than a few percent of the total). The ion transmission from both an auxiliary cathode and the filament itself was dependent on the parameters used. Maximum ion signals were obtained with a constant voltage discharge and the maximum filament current, so these parameters were used for the majority of the data. The method showed fairly good linearity in the limited concentration range studied for these experiments. The optimum operating pressure was found to be about 1.2 Torr argon, which is consistent with that used for a typical glow discharge application.

The surprising difference that was observed with this source is the cathode-to-exit orifice distance that produces the maximum ion signal. For the electrothermal source, the maximum signal was observed with the filament 3.5 mm from the ion exit orifice. This difference may be a result of the electron production from the filament, which is absent in a typical glow discharge, or the atoms in the plasma may be at a different energy level than those of the typical discharge. The positioning of the sample on the filament is a critical parameter as well, with the maximum ion signal obtained when the sample is applied at the end of the filament nearest the ion exit orifice. This method shows no significant memory effects when a blank sample is used, which is important since many analyses of this type suffer greatly from memory effects. Only binary element samples were demonstrated in the data presented here, since the elements must be in a very narrow mass range for analysis. Improvements in quantitation would be expected if internal standards were used during the analysis. Binary samples were separated by ramping the filament current, but this method requires elements that
are far apart in their atomization currents unless the power supply is computer controlled. Internal and external ETV introduction schemes were used and compared. The internal method is the preferred method, due to its simplicity and better sensitivity. However, internal ETV introduction suffers from higher relative standard deviations and the erosion of the filament material. The inconsistencies of this technique have been contributed to the continual introduction of contaminant air and water vapor with each subsequent sample. The effects of water vapor contamination will be addressed in the following chapters.
CHAPTER 3
THE EFFECTS OF WATER VAPOR ON GDMS:
STEADY-STATE WATER ADDITION

Introduction

The next two chapters of this dissertation focus on the effects of water vapor (which is always present to some extent in a glow discharge ion source) on the production of the atoms and ions that are used for analytical studies. These examinations were undertaken since the research presented in Chapter 2 was determined to be affected by the water and other contaminants that were introduced into the ion source with each subsequent sample. Also these deterring effects of water vapor content on the analytical results obtained with glow discharge are of interest. Water vapor content in the plasma might vary from run to run depending on the environmental conditions external to the mass spectrometer to which the sample was exposed. These varying experimental conditions might subsequently affect the reproducibility of analytical results.

The ion signal intensities that are detected by the mass spectrometer may be influenced through a variety of means, including the presence of impurities (such as water vapor) in the glow discharge ion source. It has been determined that it is very important to use ultra high purity sputtering gases to improve the long-term stability and accuracy of glow discharge analytical results [20]. When water vapor is present, the resultant mass spectra will contain a variety of ion
signals that are produced from water vapor or combinations of water vapor species with the analyte of interest. Water vapor may be introduced by different means, including leaks in the vacuum system, water occluded within the sample itself (e.g., a powdered material that must be compressed to form the discharge cathode), the discharge gas, or water outgassing from the surfaces of the ion source components or gas lines. This chapter reports on the effects of introducing a constant concentration of water vapor on the fundamental glow discharge processes (sputtering and ionization) and the subsequent changes in a variety of ion signal (e.g., analyte ion, Ar\(^+\), H\(_2\)O\(^+\), and H\(_3\)O\(^+\)) intensities that have been observed using a mass spectrometer.

In this chapter, the effects of water vapor were studied by adding controlled amounts of water into the mass spectrometer in a steady-state fashion. This method of addition was chosen for the preliminary studies, so that the water vapor effects may be initially characterized at a constant concentration. The effects encountered with a pulsed introduction of a small volume of water vapor and the resulting time resolved behavior of the ion signals will be discussed in Chapter 4. Understanding the time resolved behavior of ion signals while pulsing water vapor first required a thorough comprehension of the processes occurring with a steady concentration.

Once a constant concentration of water vapor was established in the ion source, the overall effects of the water vapor presence were noted. After observing the resultant effects, the ion signals were monitored to observe their changes while the water was subsequently removed and the plasma returned to
its "normal" state. This provides insight into the mechanisms occurring in the plasma when the water is initially added and the processes resulting in the plasma environment recovering to its original state. Three methods of water removal were investigated: 1) the water was pumped from the ion source by the vacuum system, 2) the water was reacted out of the ion source by using a sample cathode that actively reacts with water and removes it to the chamber walls (i.e., getter elements) and 3) the water was cryogenically removed using a liquid nitrogen cooled coil.

The effects of water on the plasma processes are important considerations when using glow discharge ion sources. The water contamination may affect the analytical results obtained with glow discharge methods by two major pathways: 1) changing the ionization mechanisms in the plasma, and 2) changing the sputter-atomization processes of the glow discharge, which results in a decreased atomic population. As mentioned in Chapter 1, ionization processes in the glow discharge rely mainly on the collisions of analyte atoms with long-lived argon metastable species (Penning ionization) [35]. Thus, any suppressing effects that water vapor has on argon metastables would result in a reduction of ion signal as measured by the mass spectrometer. Water vapor and other organic molecules in the ion source have been shown to quench the argon metastable population by an energy transfer from the metastable atom to the water or other organic molecule [86]. As the argon metastable population is decreased, the ion signal will become lower due to the loss of this ionization pathway.
The Dissociation of Water in Gas Discharges

A discussion of the dissociation of water vapor is appropriate here, since many of these dissociation products may play an active role in the reactions occurring in the glow discharge. Water vapor was initially studied in gas discharge tubes as a means of examining the free hydroxyl radical OH [87]. Initially, the final products of the dissociation of water vapor in a gas discharge at ordinary temperatures were found to consist of hydrogen, oxygen, and water only. It was later reported that the neutral OH radical was present in these systems as well [88], and hydrogen atoms as well as OH would be involved in the reactions of dissociated water vapor. It was also observed that oxygen may be formed in a discharge tube by the dissociation of OH [89], while Kaufman and Del Greco [90] found that the relative proportions of OH and O in the discharge should depend on the rate of the reaction shown in Equation (19):

\[ \text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H} \]  \hspace{1cm} (19)

This reaction has no appreciable activation energy and some \( \text{O}_2 \) was expected to be found in the discharge tube [91]. Bonhoeffer and Person suggested an overall mechanism for the reactions occurring in dissociated water vapor systems [92]. These reactions are shown in Table VI. From these results, we may expect to see reactions in the glow discharge resulting in ions from any or all of the reactants and products occurring in this mechanism. Some rate constants and reactions involving dissociated water species, such as OH and \( \text{O}_2 \text{H} \) radicals as well as atomic species such as hydrogen and oxygen, have been reviewed in the
TABLE VI. Overall Reaction Mechanism of Dissociated Water Vapor in a Gas Discharge

\[
\begin{align*}
H_2O & \rightarrow H + OH \\
H + H & \rightarrow H_2 \\
OH^+ & \rightarrow OH \\
OH + OH + M & \rightarrow H_2O + O + M \\
O + O & \rightarrow O_2
\end{align*}
\]

where M is a surface or third body.

Source: Reference [92].
literature [93]. That publication and the references therein give insight to the many reactions that may occur in a system where water vapor is present.

The products and processes of the ionization in water vapor by electron impact have been studied by some researchers as well [94,95,96]. The positive ions under study included $\text{H}_2\text{O}^+$, $\text{H}^+$, $\text{OH}^+$, $\text{H}_3\text{O}^+$, $\text{O}^+$, $\text{H}_2^+$, and $\text{O}_2^+$. Further studies were carried out on some of these ions [97,98,99] and the reactions that were proposed to lead the principal positive ions are shown in Table VII. These reactions as well as others will be expected to occur in the present glow discharge system, since the primary ionization mechanism for gaseous impurities relies on electron impact.

This section has presented an overview of some early work that studied the dissociation of water vapor in discharge and mass spectrometry systems. However, these systems failed to consider the reactions that are occurring between the water vapor species and the normal glow discharge species (i.e., the discharge gas species and the sputtered species). The following section will present an introduction to studies that have been reported more recently in glow discharge systems similar to that used in the experiments presented in this dissertation.

**Studies of Water Vapor Effects in Glow Discharges**

The focus of this section is on the interactions of water vapor species with the discharge gas as well as the cathode material. Of primary concern is the effect water vapor in the discharge chamber will have on the fundamental processes in the plasma, such as atomization (sputtering) and ionization.
TABLE VII. Principal Positive Ions Formed in Water Vapor by Electron Ionization

<table>
<thead>
<tr>
<th>Ion</th>
<th>Probable Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_3O^+</td>
<td>H_2O^+ + H_2O → H_3O^+ + OH</td>
</tr>
<tr>
<td>H_2O^+</td>
<td>H_2O → H_2O^+</td>
</tr>
<tr>
<td>OH^+</td>
<td>H_2O → H + OH^+</td>
</tr>
<tr>
<td>O^+</td>
<td>H_2O → H + O^+</td>
</tr>
<tr>
<td></td>
<td>H_2O → 2H + O^+</td>
</tr>
<tr>
<td>O_2^+</td>
<td>O_2 → O_2^+</td>
</tr>
<tr>
<td>H^+</td>
<td>H_2O → OH + H^+</td>
</tr>
<tr>
<td>H_2^+</td>
<td>H_2O → O + H_2^+</td>
</tr>
</tbody>
</table>

Source: Reference [98,99].
The effects of water in the glow discharge will be better understood by studying the reactions that occur in the plasma when water molecules are present. A variety of possible reactions involving argon and water was proposed by Lindinger in a study using a steady-state hollow cathode discharge with 0.15\% water in a balance of argon [100]. The pertinent reactions that were reported are as follows:

\[
\begin{align*}
\text{Ar} + e^- & \rightarrow \text{Ar}^* + 2e^- \\
\text{Ar} + e^- & \rightarrow \text{Ar}^{2+} + 3e^- \\
\text{Ar}^* + \text{Ar} & \rightarrow \text{Ar}_2^* + e^- \\
\text{Ar}^* + \text{H}_2\text{O} & \rightarrow \text{ArH}^+ + \text{OH} \\
\text{ArH}^+ + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+ + \text{Ar} \\
\text{H}_2\text{O}^+ + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+ + \text{OH} \\
\text{Ar}^* + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}^+ + \text{Ar} \\
\text{H}_3\text{O}^+ + e^- & \rightarrow \text{H}_2\text{O} + \text{H}
\end{align*}
\]

where $\text{Ar}^*$ indicates excited Ar.

Reactions listed in Equations (20) - (22) are related to the formation of the various argon ions that exist in the plasma, while the more direct interactions of water vapor are shown in Equations (23) - (27). It is evident from these reactions that an increase in the water concentration of the plasma will shift the reactions depicted by Equations (23) - (26) to the right side and will result in a discharge plasma enriched in $\text{H}_2\text{O}$ and $\text{H}_3\text{O}$ ions. From Equations (23) and (26), it is also evident that the argon ions, which are mainly responsible for the sputtering
processes, are being consumed by the added water. Reaction (25) was shown to proceed rapidly and for this reason the intensity of H$_3$O$^+$ is often greater than that of H$_2$O$^+$ when traces of H$_2$O are present in the plasma [101]. It was determined that H$_2$O$^+$ is formed mainly by the ion-molecule reaction shown in Equation (26) [100]. As a result of these observations, one could expect reduced sputtering of the analyte species and a mass spectrum that contains two significant ion signals at mass-to-charge ratios 18 and 19. Also, other products from the decomposition of water that were outlined above (e.g., O or OH) or water-analyte cluster species may be present in the ion source, depending on the plasma conditions and the cathode sample.

A decrease in sample atomization is another major concern as a result of the presence of water vapor in the glow discharge source. Water molecules may dissociate in the plasma leaving a large amount of hydrogen ions or other fragment ions that could decrease the analyte sputtering rate by replacing some of the argon ions in the source. A decrease will occur if the discharge current is being partially supported by these fragment ions (e.g., H$^+$) in the discharge, rather than by argon ions alone. It has been shown that the greater fraction of the current in a gaseous conductor is carried by the species with the highest mobility [3], and the mobility of the positive ions vary with mass (with lower mass ions exhibiting higher mobility) [102]. Stern and Caswell found that the hydrogen ions in a sputtering system have between 20 and 40 times the mobility of the argon ions depending on the discharge conditions [103]. When the hydrogen ions carry a large fraction of the current, they will produce a reduced sputter rate due to
their low mass [104]. Sputter yields with a variety of species have been investigated and the sputter efficiency was shown to be related to the mass of the sputtering ion, with low mass ions resulting in lower sputter yields [104]. Therefore, any small fragment species in the plasma could carry a large amount of the discharge current, but not effectively sputter the analyte.

Gough et al. [105] showed by atomic absorption that sputtering of the sample in the presence of water is not as efficient as sputtering with dry argon and will decrease the concentration of sputtered neutrals in the plasma. It was noted that the absorption of ground state Cr atoms decreased and the precision of the measurements worsened when changing from an argon gas supply with 3 ppm water to one with 17 ppm. Similar effects have also been demonstrated while introducing methane gas into the plasma and monitoring the sputtered atom population with atomic absorption [106]. It was postulated that as the methane concentration is increased in the discharge gas, more of the discharge current will be carried by the highly mobile hydrogen ions, methane ions, and other fragment ions coming from the methane molecule.

The effects of water vapor on glow discharge sputter-atomization was also investigated by Larkins in an argon discharge gas containing various amounts of water (up to 140 ppm) using atomic absorption measurements [107]. A decrease in absorbance signal was observed and the magnitude of these water induced effects varied depending on the sample being sputtered and the discharge current. At a level of 140 ppm water vapor, the reduced absorbance values varied from 12% for nickel in steel to about 77% for chromium in aluminum. These
effects were observed to be more prominent when sputtering was carried out using lower discharge currents. The decrease in the atomic population was shown to be the result of lower sample erosion rates as well as processes in the plasma such as gas-phase reactions between water molecules and fragments with free atoms.

With these detrimental effects being considered, experimental methods need to be developed that will avoid, or at least reduce, these problems. Initial steps that may be taken to eliminate water contamination are using ultra pure argon discharge gas and avoiding vacuum leaks in the mass spectrometer, although these preventive steps alone are not sufficient. Other methods that have been shown to decrease the residual water vapor concentration are the use of a cryogenic device to remove physically the water vapor and the use of gettering materials, which will chemically eliminate oxygen-bearing species and other impurities when sputtered into the discharge chamber [108]. These methods will be elaborated upon further in a later section of this chapter.

Few in-depth studies have been performed to observe the effects of water vapor using mass spectral methods. Some initial studies were performed in this laboratory by Loving and Harrison to demonstrate the changes occurring in an iron glow discharge as the water content of the plasma was changed [36]. The study that is described in this dissertation was conducted also to observe the effects of small amounts of water vapor contamination on the ion signals detected with a quadrupole mass spectrometer. These fundamental studies give insight into water reactions that exist in the plasma and the possible changes in ion
signals as a result of changing the water concentration. The immediate effects of water vapor contamination will be demonstrated with mass spectra obtained first under normal conditions and then with the steady state addition of a small amount of water vapor. The resulting effects on the neutral analyte species population as well as the argon metastables were studied by atomic absorption. The changes that occur upon removing water vapor were studied by first maintaining a steady-state water vapor concentration in the ion source and then removing the water vapor. The changing ion signals were then monitored with time as the water is removed. Experiments were also conducted to explore the effects encountered when using three different metal matrices (titanium, iron, and copper) that have varying reactivity toward oxygen, which should indicate the influence that water has on these elements.

Experimental

These experiments were performed on the quadrupole mass spectrometers that were described in Chapter 1. The modifications made to the mass spectrometers for the water experiments will be described in detail below. The cathode materials used in the experiments were Ti [Aldrich Chemical Co.; Milwaukee, WI; #34,885-6, 99.97% pure], stainless steel [National Institute of Standards and Technology; Gaithersburg, MD; SRM 1265, >99.9% Fe], and Cu [Johnson Matthey Chem. Ltd.; Royston, England; 99.999% pure]. The titanium and copper were purchased as 2 mm wires and were cut to an appropriate length to fit the direct insertion probe. The iron sample was machined into 2 mm pins from a bulk disk, the length of the pin being determined by the thickness of the
standard disk. A five millimeter section of the sample was left exposed to the negative glow for sputtering. The gas used in these experiments was 99.999% pure argon [Liquid Air Corporation; San Francisco, CA] and the discharge pressure was maintained at approximately 1 Torr.

Studying the effects of water vapor first required a means of introducing the water in a reproducible and steady fashion. An introduction valve assembly, shown in Figure 41, was constructed to allow the water vapor to bleed into the ion source in a constant and controllable rate. The assembly is made up of a shut off valve [Whitey; part# SS-3NBS4], a needle valve [Whitey; Highland Heights, OH; part# SS-21RS4], and a water reservoir, connected in series to the mass spectrometer. The water reservoir is made up of a 0.75" diameter glass bulb at the end of the assembly. It is attached to the assembly by a 0.25" O-ring connector [Cajon; Macedonia, OH; part# SS-4-UT-1-2]. The entire assembly is then attached to the ion source by a 0.25" Cajon connector welded into the center of a 2.75" flange (MDC Vacuum Products; Hayward, CA).

The water vapor concentration was determined using a dewpoint analyzer [Shaw Moisture Meters; Bradford, England; Model SDA] to the discharge ion source. Since the moisture analyzer requires a flow of the gas to be measured across the sensor wire, the sensor was placed in line between the glow discharge ion source and a vacuum pump to provide the necessary flow of the discharge chamber gases. The argon gas flow into the ion source was adjusted to maintain the source operating pressure of 1 Torr. Figure 42 shows a block diagram of this experimental setup. The sensor is constructed from a small wire composed of an
Figure 42 Block diagram of the experimental set-up to measure the water vapor pressure in the GDMS ion source.
aluminum core, a hygroscopic aluminum oxide dielectric layer (a few microns in thickness), and a thin covering of porous gold film. The pores of the film and oxide layer are very small and are specific to the size of the water vapor molecule [109]. The oxide layer will quickly (~ 30 s) reach equilibrium with the water vapor pressure, which is proportional to the dewpoint temperature. The meter readout is the dewpoint of the flowing gas in degrees Celsius, which can be subsequently converted to the water vapor pressure in mm Hg (Torr) [109].

The cryogenic coil studies were performed in the Extrel ion source, which is constructed from a standard six way cross with 2.75" flanges, as described in Chapter 1. The source design is depicted in Figure 43, which shows the spatial relationship of the cryogenic coil to the sample pin and the negative glow. This coil was constructed in the University of Florida Chemistry Department machine shop from 0.125" stainless steel tubing welded to a double sided vacuum flange [MDC Vacuum Products; Hayward, CA; part # 140009] to accommodate the introduction of both the coil and the direct insertion sample probe simultaneously. An insulated liquid nitrogen container is attached to the top of the flange, and the flow through the coil relies on the liquid being drawn through by gravity. A mechanical vacuum pump may be attached to the coil exit port to maintain the flow of liquid nitrogen, if required.

**Results and Discussion**

**Effects of Water Vapor on Mass Spectra**

The initial indications of the effects that water vapor has on a glow discharge mass spectrum can be observed by collecting a spectrum while
Figure 43  Schematic diagram of the Extrel ion source with the cryogenic coil.
bleeding a small amount of water vapor into the ion source. Figure 44 shows two mass spectra that reveal the differences before and after water addition. In Figure 44A, the mass spectrum of a titanium sample is shown after sputtering for about 30 minutes (discharge conditions: 1000 V, 3.8 mA), which is a sufficient sputtering time to clean the pin surface of any oxide layer and obtain a steady state analyte ion signal. The observed spectrum demonstrates the reduced magnitude of the interfering species present in the ion source. With a titanium cathode, the oxygen-containing gaseous interferants are efficiently removed by the gettering action of the titanium. The predominant species that appear in the spectrum are $H_3^+$, ArH$^+$, and $^{48}\text{Ti}^+$. $H_3^+$ is often present in glow discharge spectra and is thought to form by the following reactions [110,111]:

\[
H_2 + e^- \rightarrow H_2^+ + 2e^-
\]  \hspace{1cm} (28)

\[
H_2 + H_2^+ \rightarrow H_3^+ + H
\]  \hspace{1cm} (29)

If the ion source is kept clean, the intensity of $H_3^+$ will normally continue to decrease over the sputtering period. The $H_2$ content in the ion source is normally low, but may arise from a variety of sources. The most prominent source of hydrogen in a discharge system is from the dissociation of water vapor [104]. Water vapor can evolve from the sample during sputtering, since even ultra pure metals can contain gaseous impurities [112]. Water vapor also may be introduced into the source with room air that is brought in with each sample and will result in an increase of hydrogen [102]. Govier and McCracken observed the correlation between water vapor pressure and hydrogen pressure in a sputtering
Figure 44  Mass spectra of a titanium pin.  A) Typical spectrum taken after 30 min of sputtering.  B) Spectrum taken with 0.05 Torr of water being introduced.
system [113]. Upon discharge initiation the concentration of each was relatively high but decreased with the sample sputtering time. Another possible source of hydrogen that has been considered is from back diffusion from the pumping system [114], and the inability of some pumps (especially turbomolecular) to remove a low mass species such as hydrogen [115].

In sharp contrast, the spectrum shown in Figure 44B was obtained about 5 min after opening the water introduction valve that allowed approximately 0.05 Torr of water vapor into the ion source (discharge conditions: 1000 V, 2.0 mA; note the decrease in current with the added water content while the voltage was held constant). The glow discharge current has been observed in these studies to be inversely proportional to the amount of water vapor that is present in the ion source as the voltage is kept constant. Previous studies performed with water addition in which the current was held constant resulted in an increased voltage [108], agreeing with the present voltage-current behavior. The dramatic differences in the ions produced with and without water contamination are obvious from these figures. As discussed earlier, adding water to the system will shift equations (23) - (26) toward the right, giving a mixture of H₂O and H₃O ions being formed in the ion source. The predominant ions with water addition are those of the water species as well as a small contribution from molecular oxygen at m/z 32. This species arises from the electron impact ionization of O₂ that is present upon dissociation of water vapor, as discussed earlier. On this scale, no ion signal is observed for the analyte elements and the intensities of the other peaks have also been reduced. This reveals the significant quenching effect that
the water vapor has on the ion analyte signals detected from the glow discharge source.

**Effects of Water on Neutral Species**

Because ion signals do not supply information about sputtering directly, it is important to study the effects of water vapor on some neutral species in the plasma. The atomic absorption measurements performed in these experiments indicate how the neutral population in the ion source changes during the addition of water vapor, since absorbance values are directly proportional to the concentration of the ground state species. Also, the absorbance of the argon metastable may be monitored to give an indication of its population in the ion source. Argon metastables are important since they provide the path for Penning ionization, which is one of the predominant ionization mechanisms for GDMS. Table VIII lists the effects of the addition of water on absorbance measurements taken on the argon metastables (\( \lambda = 811.5 \) nm) as well as the titanium atoms (\( \lambda = 365.3 \) nm). These data show the reduction in the population of the metastables due to the quenching effects of the water as well as the decrease in the sputtered titanium atoms. These effects will occur as some of the argon ions are being replaced by water fragments and the sputtering becomes less efficient as previously discussed. Both reductions will contribute to the decrease in the analyte ion signals that were observed in Figure 44B. These measurements indicate that any discharge species that rely on sputtering and subsequent Penning ionization will be reduced upon the addition of water into the system.
Table VIII. Changes in the Atomic Neutral Population of Titanium and Argon Metastable Species in the Plasma

<table>
<thead>
<tr>
<th>Discharge Conditions</th>
<th>Ti Absorbance</th>
<th>Ar* Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Torr Ar</td>
<td>0.146</td>
<td>0.070</td>
</tr>
<tr>
<td>1 Torr Ar + 0.05 Torr H₂O</td>
<td>0.012</td>
<td>0.016</td>
</tr>
<tr>
<td>% decrease upon adding H₂O</td>
<td>92</td>
<td>78</td>
</tr>
</tbody>
</table>
Effects of Water on Various Plasma Species

The following experiments were performed to investigate the changes that occur in the plasma species of the glow discharge as water is removed from the ion source. This was accomplished by first obtaining a steady-state water concentration in the ion source by opening the water introduction assembly shut-off valve, which produces conditions similar to those used when Figure 44B was obtained. After reaching a steady-state condition, the water valve was then turned off and the water vapor allowed to pump (or react, depending on the cathode material being used) out of the system. Figure 45 shows the behavior of the water vapor pressure during these experiments, as measured by the moisture meter. The initial value of the water vapor pressure was approximately 0.025 Torr, which is 2.5% of the total discharge pressure. The behavior of the water concentration shown in this figure was reproducible and did not vary significantly during any of the following experiments, even with the use of different cathodes. As will be seen later, all of the major changes in the ion signals under investigation were observed in a period after the water vapor concentration had leveled off as indicated by the measuring device.

Figure 46 shows the time-dependent behavior of four species of interest from a titanium discharge (H$_2$O$^+$, H$_3$O$^+$, Ar$^+$, and Ti$^+$). This set of data was obtained during the same time frame as that used for Figure 45. The H$_2$O$^+$ signal remains mostly constant, while the H$_3$O$^+$ signal steadily decreases up to a "transition point" where both ion signals quickly fall to zero intensity. This trend would be expected in relation to the water reactions that were described by
Figure 45. Plot of the changing water vapor pressure over the time frame of the experiment. The water introduction is turned off at $t = 2.8$ min.
Figure 46 Changes in ion signals from a titanium pin as the water vapor is removed from the ion source. ●-H$_2$O$^+$; ■-H$_3$O$^+$; △-Ar$^+$; ◆-Ti$^+$. 
Equations (23) - (26). Conversely, as the water is removed, the Ar$^+$ and Ti$^+$ slowly begin to increase. At $t = 25$ min, these ion signals quickly rise to a plateau intensity that would be comparable to the normally expected values obtained using a dry ion source. This "transition point" appears to be a time when the plasma changes from an oxidizing plasma that supports oxygen-containing and dissociated water vapor species to a more reducing atmosphere that is dominated by the elemental species. The results shown in Figure 46 would appear to be a result of changes in both the atomization and ionization processes in the plasma as the water is removed from the ion source. These types of "redox" transitions and "titration-like" curves have been demonstrated by Roth when monitoring the changes in sputtering yields of titanium using 11 keV argon ions in a residual gas containing various amounts of oxygen, hydrogen, and nitrogen contaminants [116]. It was shown that as the partial pressures of any of these three contaminant gases were increased, a transition will be observed in the sputter yield. The sputter yield was shown to go rapidly from a level observed with argon alone to a plateau level that is significantly lower. This transition was observed to occur over a small change in partial pressure. Thus, the sputter yield profile, with changing concentrations of contaminant species, revealed a similar "transition point" as observed in Figure 46.

Effects of Water on Various Cathode Materials (Matrix Effects)

Another study of interest involved the observation of the differing effects that water has on various cathode materials. This study is important to determine whether different elements exhibit different behavior with respect to the water
content in the ion source. This could make analytical determinations of some elements more difficult if a particular element is found to be more greatly affected by the water content of the plasma. Thus, the analysis of alloy materials may prove difficult if the elements making up the alloy have vastly different interactions with the water vapor.

The materials studied for comparison were Ti, Fe, and Cu. These three elements exhibit differing oxide bond strengths, listed in decreasing order: Ti-O, 159.3±1.5 kcal/mol; Fe-O, 97.7±3 kcal/mol; Cu-O, 65.2 kcal/mol [85]. The oxide bond strength will contribute to the species observed in a glow discharge mass spectrum and is of interest in the current studies since the introduction of water vapor into the plasma should produce an oxidizing environment [108]. The correlation between the oxide bond strength and the observed species in a glow discharge has been previously studied. It has been observed that the ratio of the population of dimer species to their single atoms will increase with the dimer binding energy [117]. Coburn and coworkers [118] focussed on the species produced from oxide targets and found that with increasing M-O bond energy that the ratio MO⁺/(M⁺ + MO⁺) observed with a quadrupole mass spectrometer also increases. The M-O bond strength will be a contributing factor in the present studies. With the relatively high concentration of water in the plasma, M-O species will be formed both on the sample surface and in the gas phase. With the introduction of water the cathode will form an oxide layer on its surface and in the initial sputtering period the loss in M⁺ signal may be the result of the formation of MO⁺ species. This effect will be more
prominent with reactive metals. However, metal-oxide bond strength is not the only influencing factor as there are many ion molecule reactions occurring in the plasma to change its characteristics. These considerations will be discussed in detail later.

Copper is of interest since it has been observed experimentally in this laboratory to produce continually noticeable amounts of water ion signals even after long sputtering times. This might be expected since copper atoms will not react as readily with oxygen species to remove them from the plasma. Thus, with Cu it is imperative to use a high purity discharge gas to obtain a mass spectrum with low levels of water contaminants. On the other hand, a titanium cathode will result in a fairly clean spectrum even without using ultra high purity gas due to its strong oxide bond strength that allows it to react with these species and remove them from the plasma. However, the time required to achieve this condition may take a long sputtering period. This will depend on the extent of the oxide contamination on the surface of the cathode. If the cathode is being sputtered in a clean environment that suddenly encounters a small increase in water content, the recovery would occur quickly since the oxide layer is not allowed to form extensively on the surface of the cathode. On the other hand, if the cathode is exposed to extensive oxidation before beginning to sputter, then the time required to produce a "clean" spectrum would take longer.

Figure 47 shows the matrix ion signals that were obtained as the water was removed from the source while sputtering these three samples in separate runs. Again, the water concentration decreases over the time frame in a manner similar
Figure 47  Changes in ion signals of various matrices as the water vapor is removed from the ion source. •-Fe⁺; ■-Ti⁺; ▲-Cu⁺.
to that depicted in Figure 45. Figure 47 will be discussed in three different stages with respect to time as follows: 1) the initial stage before and just after the water valve is closed off, 2) the intermediate stage where ion signal transitions are occurring, and 3) the final stage after the transitions where the ion signals again reach a steady state intensity and appear to be of a magnitude similar to that obtained prior to the water addition.

The initial stage exhibits ion signals that are at or very close to zero intensity. The only observable signal at the beginning of the data collection is from copper. During this period, the surface of the individual cathodes should be essentially oxidized due to the constant presence of the water vapor. The copper exhibits a small ion signal in this initial stage probably because its surface is not as readily oxidized due to its lower oxygen reactivity. After the water is turned off (at t = 2.8 min), the copper signal begins to increase more quickly than the other two (iron and titanium), suggesting that the relatively thinner oxide layer is being removed more readily and the copper atoms in the sample are beginning to sputter sufficiently enough to produce more of an ion signal. Also, after the water is turned off the iron pin just begins to produce an ion signal. At a time of about 17 min, the copper signal has reached its plateau value, while the ion signal intensities of the titanium and iron remain very small. This again reflects the lower oxide bond strength of the copper and its relative ease for being sputter removed. Thus in this first stage of surface cleaning, the species with the lower oxygen reactivity will begin to sputter sooner due to the inability to retain an oxide layer on the surface. It should be noted that over the period of 0 - 20 min the
appearance time and magnitude of the ion signals are what would be predicted when considering surface oxidation and its removal. The lower the oxidation of the surface the quicker sputtering will begin to remove efficiently the sample atoms. This will result in a faster appearance and a higher ion signal during this period.

In the intermediate stage, the "titration-like" curve is again observed with the titanium sample and occurs at the same time observed in Figure 46. The iron signal shows a similar behavior, but its "transition point" occurs later (at $t = 35$ min). This demonstrates the ability that iron and titanium cathodes have to produce a "clean" discharge environment after some amount of sputtering. However, it takes longer to achieve these conditions when using an iron cathode since its ability to remove the water contaminants chemically is less efficient than titanium. This delayed occurrence of the transition point agrees with the lower oxide bond strength of iron. During this intermediate time where titanium and iron are quickly increasing, the copper ion signal is still maintaining its plateau value and shows no similar "transition point." Once the water source is turned off and the surface sputtering has begun, gas-phase reactions seem to play a more significant role as to which species will reach its "transition point" first. It is the species with the highest oxide bond strength that will react with the water species more efficiently and contain them for subsequent removal to the chamber walls. Therefore, even though the iron ions were detected first, they were not able to clean up the ion source by gas-phase reactions as quickly as the titanium, which removes impurities by its gettering action. Notice that in this middle stage the
copper ion signal shows no improvement since its ability to react with the water species and oxygen is limited by its lower reactivity.

The water ion signals for these experiments are not shown on this graph. The water ion signals for titanium and iron produce a similar trend as those illustrated in Figure 46, and fall to zero or low intensity at their corresponding "transition points." The water ion signals with the copper cathode show a decreasing trend similar to the water concentration, but never pass through a transition point or fall to zero intensity since copper is poor in removing the water species. For comparison, during the final stage of this experiment a titanium or iron mass spectrum taken at 45 minutes would show a clean mass spectrum with no H₂O or H₃O ion signals. This is due to their relatively high reactivity that has allowed the water species to be reacted out of the chamber. A copper spectrum taken at a similar time would still have a small contribution from the water species. Thus, in the final stages, the different reactivities of these elements are apparent by the overall signal that was achieved over the course of this experiment. The behavior of water species ions and other ions of interest will be considered further in the next section.

As demonstrated above, water removal may be accomplished by sputtering elements that will react with the water and remove it from the ion source. This form of water removal will depend on the material that is being sputtered in the plasma. Water removal due to this gettering ability can change the mass spectrum that is obtained and the amount of time required to produce a "clean" mass spectrum. Gettering elements have been observed to produce varying
effects on the removal of oxygen-containing species and other impurities from the plasma environment with tantalum and titanium being shown to be quite effective in producing a lanthanum atomic signal from a lanthanum oxide sample [119]. Therefore, the cathode material may be chosen appropriately to maximize the amount of water removed by the sputtering processes, if a particular glow discharge experiment allows for this flexibility.

**Effects of Water on Plasma Species in Different Matrices**

In this section, the behavior of other plasma species will be discussed while observing the ion signals in the same time frame as that used in the experiments of the previous two sections. This section will address and discuss the ion signal behavior of various plasma species ion signals in the three matrices described above. The ions that are of interest include: 1) $\text{H}_3^+$, 2) $\text{O}^+$, 3) $\text{OH}^+$, 4) $\text{H}_2\text{O}^+$, 5) $\text{H}_3\text{O}^+$, 6) $\text{Ar}_2^+$, 7) $\text{N}_2\text{H}^+$ and $\text{COH}^+$, 8) $\text{Ar}^+$, 9) $\text{ArH}^+$, and 10) $\text{Ar}_2^+$. The following discussion will be separated into groups of ions that exhibit similar behavior in their plasma reactions.

**Hydrogen, Oxygen, and Hydroxide.** Monitoring the hydrogen ions (at m/z = 3), the oxygen ions (at m/z = 16), and the hydroxide ions (at m/z = 17) in the plasma should give an indication of the water dissociation products that are present in the glow discharge. These three species are the main products of water dissociation, as discussed earlier. As shown in Table VI and Table VII, there is a good chance that $\text{H}_2$ is present in the water vapor equilibrium, which would lead to the corresponding ion signal observed at m/z = 3 by the reactions shown in Equations (28) and (29). Also, any free oxygen atoms that are formed
could be ionized to form the $O^+$ at $m/z = 16$. The hydroxide species was discussed earlier to be present as an ion under electron ionization conditions and as a neutral radical. This species has been studied with respect to its ionization in a mass spectrometer and its ionization energy was found to be about 13.18 eV [120]. The ion signals of these three species are shown in Figures 48, 49, and 50 with the three cathodes discussed above. All three ion signals show a similar behavior, which would indicate that they are involved together in an equilibrium process. These signals show a fairly constant ion signal over the entire run with the copper cathode, which has lower reactivity. With the titanium cathode, these species show little signal before the transition point and have a short lived spike at this point. With iron, the signals have a sharp increase at the transition point and then show a gradual decrease over the remainder of the experiment. The sharp increases at the transition points may correspond to the water species equilibrium shifting to the more dissociated state in the plasma or where these species may be better ionized as the water content is reduced. Earlier research of water vapor in gas discharges has presented similar results, where the water ion is no longer stable in the discharge and the ions of its dissociation products become the predominant species. According to Laidler [121], the appearance of $OH^+$ is due to the formation of an $H_2O^+$ state that is unstable with respect to $H$ and $OH^+$. When this condition is present the overall process is represented as [121]:
Figure 48  Changes in the $\text{H}_3^+$ ion signal in various matrices as the water vapor is removed from the ion source.  •-Fe matrix; ■-Ti matrix; ▲-Cu matrix.
Figure 49  Changes in the \( \text{O}^+ \) ion signal in various matrices as the water vapor is removed from the ion source.  •-Fe matrix; ■-Ti matrix; ▲-Cu matrix.
Figure 50 Changes in the OH$^+$ ion signal in various matrices as the water vapor is removed from the ion source. •-Fe matrix; ■-Ti matrix; ▲-Cu matrix.
\[ e^- + H_2O \rightarrow H_2O^+ + 2e^- \rightarrow H + OH^+ + 2e^- \quad (30) \]

Laidler also proposed a similar mechanism for the appearance of O\(^+\) when this unstable state of H\(_2\)O\(^+\) with respect to H\(_2\) and O\(^+\) is encountered [121]:

\[ e^- + H_2O \rightarrow H_2O^+ + 2e^- \rightarrow H_2 + O^+ + 2e^- \quad (31) \]

A similarly unstable state of the water ion also may be encountered that leads to H\(_2^+\) and O by a reaction similar to those shown above. This ion is a precursor to the H\(_3\) ion that is observed in the glow discharge source. All of the reactions discussed here are considered in more detail in the paper by Laidler, and potential energy curves are presented to demonstrate that these reactions may proceed energetically.

Therefore, when this condition occurs in the discharge it is likely that the intensity of the H\(_2\)O\(^+\) signal will sharply decrease while ion signals of hydrogen, oxygen and hydroxide will become predominant. This is in agreement with the results discussed above and shown in Figures 48, 49, and 50. Consequently, the titanium will react in the gas phase with these contaminant species, which may result in the quick loss of these ion signals after their appearance. Since the iron pin does not exhibit as large of a gettering capability to clean up impurities as titanium, these ion signals will slowly decrease as the contaminant species are removed by the vacuum system or to the chamber walls. Note that all of these ion signals have a relatively low magnitude (less than 0.6 V) in the mass spectrometer.
Water and protonated water. As mentioned before, the ion signals at m/z 18 and 19 will give a direct indication of the water content in the plasma, since the total water in the plasma is an equilibrium between H$_2$O$^+$ and H$_3$O$^+$. The ion signal H$_2$O$^+$ was proposed to result both from electron ionization (see Table VII) and by charge exchange with an argon ion as shown in Equation (26). On the other hand, H$_3$O$^+$ comes from the reactions in Equations (24) and (25). Mann et al. found the intensity of the H$_3$O$^+$ signal was proportional to the square of the water vapor pressure [98]. Figure 51 shows a plot of the H$_3$O$^+$ signal obtained with the copper cathode versus the square of the water vapor pressure observed by the moisture meter. This is in agreement with the findings of Mann and co-workers. The data for the copper cathode are shown here since it is considered to react the least with the water vapor in the discharge. The results are in agreement with those observed by Mann et al., since this plot is linear throughout most of the measured range. The H$_3$O was considered to form through Equation (25) as well as the following by Mann et al.:

$$H_2O^* + H \rightarrow H_3O^*$$  \hspace{1cm} (32)

Of these reactions, they concluded that Equation (32) is more likely when considering only energetic grounds. However, the limiting factor for that equation is that the hydrogen atom concentration may be too low for it to be significant. Formation of H$_3$O$^+$ also may occur via the collision of two metastable water molecules as shown below [36]:

$$H_2O^* + H_2O^* \rightarrow H_3O^* + OH^-$$  \hspace{1cm} (33)
Figure 51
Correlation between the $\text{H}_3\text{O}^+$ ion signal in a glow discharge plasma and the square of the vapor pressure.
The ion signal response for \( \text{H}_2\text{O}^+ \) (see Figure 52) and \( \text{H}_3\text{O}^+ \) (see Figure 53) in the discharges of the three cathodes discussed above have been investigated. The ion signals from both of these species show similar trends. With the copper cathode, both ion signals gradually fall over the period from 0 - 12 min, where they eventually come to a fairly constant plateau value, following the \( \text{H}_2\text{O} \) vapor pressure trend. For the iron and titanium cathodes the \( \text{H}_2\text{O}^+ \) signal is fairly stable until the transition point is reached. At this time, the ion signals quickly decrease. The \( \text{H}_3\text{O}^+ \) signal shows a gradual decrease up to the transition point where they fall to zero intensity. This is the expected trend, and was shown in Figure 46.

Protonated nitrogen and carbon monoxide. These species are monitored because when the discharge is contaminated by air and moisture they are almost always present in a large quantity. Thus, these species will give an indication of the overall cleanliness of the plasma. Also, with the usually high amount of hydrogen in a "dirty" system, the ion signals from these species are of larger magnitude than \( \text{m/z} = 28 \) for \( \text{N}_2^+ \) and \( \text{CO}^+ \). The ion signals obtained for these species with each cathode are shown in Figure 54. In all of the runs, the ion signals of these species are zero before about 5 min. This may be because they are not efficiently ionized in the presence of the large amount of water vapor that is in the plasma. After this period, the ion signal initially increases with each cathode. For copper, the signal maximizes and then begins to decrease as the contaminants are slowly removed. With titanium, the signal begins to increase, but rapidly falls to zero at the transition point, which is probably a result of the gettering action of the titanium. With iron, the signal increases at the transition
Figure 52  Changes in the $\text{H}_2\text{O}^+$ ion signal in various matrices as the water vapor is removed from the ion source.  ●-Fe matrix; ■-Ti matrix; ▲-Cu matrix.
Figure 53  Changes in the $\text{H}_3\text{O}^+$ ion signal in various matrices as the water vapor is removed from the ion source.  •-Fe matrix; ■-Ti matrix; ▲-Cu matrix.
Figure 54 Changes in the $N_2H^+$ and $COH^+$ ion signals in various matrices as the water vapor is removed from the ion source. ●-Fe matrix; ■-Ti matrix; ▲-Cu matrix.
point and then gradually falls. This increase at the transition point also may reflect a change in ionization at this time. This is similar to that observed with the hydrogen ions in Figure 48 and shows the lack of iron's ability to remove contaminants with gas-phase reactions.

Argon species. The argon content in the plasma is probably an equilibrium between the $\text{Ar}^+$, $\text{Ar}^{2+}$, $\text{Ar}_2^+$, and the $\text{ArH}^+$ species. The $\text{Ar}^+$, $\text{Ar}^{2+}$, and $\text{Ar}_2^+$ are usually formed through the reactions shown in Equations (20) - (22). The reactions to produce $\text{ArH}^+$ have been studied [122] and the most likely reactions include Equation (23) as well as:

$$\text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H} \quad (34)$$

$$\text{Ar}^+ + \text{H} \rightarrow \text{ArH}^+ + \text{e}^- \quad (35)$$

Each of these reactions has been shown to proceed rapidly and from Equation (35) it seems that $\text{ArH}^+$ may be formed by a process requiring much less energy that required to ionize argon. Thus, when traces of hydrogenous impurities are present in the plasma the intensity of $\text{ArH}^+$ is typically greater than $\text{Ar}^+$ [36]. However, Equation (34) will only predominate when there are appreciable amounts of $\text{H}_2$ in the plasma. As shown in Tables VI and VII, $\text{H}_2$ may result from water dissociation.

These four ion signals are shown in Figures 55, 56, 57, and 58, respectively. Each of these ion signals follows the same general trend, indicating their coupled involvement in the plasma equilibrium. In copper each of these species shows a gradual increase followed by a plateau as the plasma is cleaned.
Figure 55
Changes in the Ar⁺ ion signal in various matrices as the water vapor is removed from the ion source. ■-Fe matrix; ▲-Ti matrix; ▢-Cu matrix.
Figure 56: Changes in the $\text{Ar}^{2+}$ ion signal in various matrices as the water vapor is removed from the ion source. ■ - Fe matrix; ▲ - Ti matrix; ▲ - Cu matrix.
Figure 57  Changes in the $\text{Ar}_2^+$ ion signal in various matrices as the water vapor is removed from the ion source.  •-Fe matrix; ■-Ti matrix; ▲-Cu matrix.
Figure 58  Changes in the ArH+ ion signal in various matrices as the water vapor is removed from the ion source.  • Fe matrix; □ Ti matrix; ▲ Cu matrix.
up, which is similar to observations made for other species above. For the
titanium, the signals show a sharp increase at the transition point and then a
constant plateau value. A spike is observed with Ar⁺, Ar₂⁺, and ArH⁺ and may
result from the equilibrium with the water dissociation products, which shows a
corresponding spike. This would occur since the water content in the plasma will
affect the argon ion concentration as shown in Equations (23) and (26). These
rapid gas-phase changes are probably enhanced by the gettering effects of the
titanium. With the iron cathode, the ion signals show a shifting increase to a
plateau value at the transition point as well.

Removal of Water with a Cryogenic Coil

As mentioned previously, a coil was constructed to house liquid nitrogen
and serve as a water sink inside the ion source plasma environment. This will
allow for the rapid removal of water vapor and any other species that freeze at a
temperature higher than that of the liquid nitrogen (boiling point: -195.8 °C). The
immediate benefits of using liquid nitrogen cooling can be observed in Figure 59.
Figure 59A was obtained with 0.05 Torr of water being bled into the ion source
in a steady state fashion as was true in earlier experiments. The sample used to
demonstrate this effect was an iron pin and the spectrum obtained with the
addition of water is very similar to that shown in Figure 44B for water added to a
titanium sample. The dominating species are the expected ion signals from H₂O⁺
and H₃O⁺, as predicted by Equations (23) - (26), as well as a contribution from
O₂⁺ at mass-to-charge 32. The liquid nitrogen was then added to the reservoir
and allowed to flow through the coil for about ten minutes while continuing the
Figure 59  Mass spectra of an iron pin. A) Spectrum taken with 0.05 Torr of water being introduced. B) Spectrum taken with 0.05 Torr water introduction and liquid nitrogen cooling.
introduction of water vapor into the chamber. The spectrum in Figure 59B was then taken and the results clearly may be seen. The cryogenic coil has effected the removal of water vapor and shifted the equilibrium of Equations (23) - (26) to the left. As a result, more argon ions are available for sputtering, producing a mass spectrum that is dominated by the sputtered species.

One disadvantage of this method may occur if the analysis takes a long time (more than 30 min or so). After liquid nitrogen is added to the coil, the water will begin to freeze out and deposit onto the coil surface. At some later time, depending on the plasma conditions, the coil will become covered with water crystals and the water will reach an equilibrium between the gas phase in the cell and the solid phase on the coil. At this point, the pressure in the discharge chamber will begin to rise slowly. When this condition is reached the analysis must be suspended until the coil reaches ambient temperature and the water vapor is pumped out of the ion source. The time required to reach this point will depend on the water content in the plasma, the size of the coil, and the ability to flow fresh liquid nitrogen through the device continuously. A different liquid nitrogen introduction system is under current development in this laboratory to alleviate the problems of a stopped-flow condition by applying a pressurized supply of liquid nitrogen on the inlet end of the coil.

Conclusions

This chapter has demonstrated the effects that water vapor will have on the plasma processes of the glow discharge as well as some methods to aid in its control and removal. As was demonstrated earlier, water vapor effects in the
plasma can occur to varying degrees depending upon the cathode material that is used, the purity of the discharge gas, and the integrity of the vacuum system. The reduction in ion signal observed with the mass spectrometer is most likely due to a combination of inefficient sputtering, oxidation of the sample surface, loss of analyte atoms through gas-phase reactions, and quenching of argon metastable atoms that are responsible for ionization of the analyte atom. Many surface and gas-phase reactions are occurring in the ion source as the water vapor content is lowered in the plasma. It was found that during the initial period, after the steady state introduction of water vapor was suspended, the greatest factors were attributed mostly to the surface interactions of the cathode. Elements with a greater reactivity toward the water in the ion source will form a more tenacious oxide layer and will result in a longer period of time before an ion signal appears for a sputtered species. Once sputtering is initiated and the surface begins to be cleaned, then gas-phase reactions seem to dominate. In this realm, the elements that are more active toward water vapor species will react with them and remove them from the system, resulting in a cleaner spectrum. A variety of gas-phase reactions are occurring in the system and these were discussed. Water dissociation products and hydrogenated species (i.e., N$_2$H and COH) show similar effects and are considered to be in an interactive equilibrium with one another. The same is true for the various argon species in the plasma that exhibit very similar behavior toward the water vapor content in the plasma. The use of a liquid nitrogen coil was demonstrated to alleviate the effects of added water
vapor by freezing out the contaminants and will result in a mass spectrum that is dominated by the elemental ion signals.

The effects studied in these experiments would become important in the analysis of an alloy or other sample that contains a variety of elements. Since ion signals of different elements are affected to different degrees in the presence of water, calibration data for quantitative analysis (e.g., RSF values) that are obtained at unknowingly different water concentrations in the plasma can no longer be reliably used. Therefore, it is especially crucial that the water content in a glow discharge ion source be controlled to a constant and minimal level for quantitative analysis.
CHAPTER 4
THE EFFECTS OF WATER VAPOR ON GDMS: PULSED WATER ADDITION

Introduction

This chapter continues to explore the reactions and interactions of water vapor in the glow discharge plasma. As discussed in Chapter 3, water vapor that is present in the glow discharge ion source will have a variety of effects on the processes that are occurring in the plasma. These effects were determined to be detrimental to both the analytical studies of the sputtered species and the fundamental processes occurring in the plasma. This is because water vapor in the plasma will decrease the amount of sample sputtering as well as quench argon metastable atoms that are responsible for Penning ionization. The experiments presented in Chapter 3 were performed by introducing a relatively large quantity of water to the glow discharge plasma. In those experiments, the water vapor was introduced in a steady state fashion, affecting not only the processes occurring in the gas phase, but the interactions on the sample surface as well. When a constant amount of water vapor was bled into the ion source, the time required to begin detecting matrix ions was correlated to the metal-oxide bond strength of the cathode material. This is because the relatively large amount of water vapor introduced into the source with this method will cause surface oxidation of the cathode as well as interactions in the gas phase.
The difference in the experiments presented in this chapter is that the water vapor was pulsed into the discharge in short bursts. This allowed a small and controllable amount of water vapor to be introduced into the glow discharge plasma. These experiments were designed to provide further insight into the transient changes that occur in the plasma upon an immediate and short lived change in the water vapor content. Also, since the amount of water vapor that is introduced into the plasma is small, the recovery time for system re-equilibration is shorter than in the previous experiments. This method of water introduction also should minimize the cathode surface oxidation that was discussed in Chapter 3. The interactions of the pulsed water vapor should affect gas-phase processes the most with this experimental scheme. It has been noted that when sputtering a reactive target material (such as a getter, which exhibits efficient gas-phase reactions toward oxygen-containing molecules), water vapor and oxygen species are often not observed, even when deliberately introduced [102].

Experimental

The only difference in the experimental scheme for these studies that has not been discussed previously is the pulsed solenoid injection valve and its controlling circuits. The block diagram for the pulsed introduction of water vapor into the ion source is shown in Figure 60. This water injection valve is mounted onto a 2.75" flange and may be connected to either mass spectrometer. A diagram of the solenoid valve mounted to the ion source of the Extrel instrument (six-way cross) is shown in Figure 61. A pulse generator (Hewlett-Packard Model
Figure 60  Block diagram of the pulsed solenoid valve water introduction system.
Figure 61  Schematic diagram of the pulsed solenoid injection valve on the Extrel ion source.
3325A) was used to trigger the control box, which in turn initiated the injection valve power supply to open the solenoid valve. The solenoid injection valve used in these studies was purchased commercially (General Valve Corporation, Series 9; Fairfield, NJ). The valve was powered by the control box, which contained a +28 V dc power supply. This control box was built in the University of Florida electronics shop for this specific purpose. The pulsed solenoid could be operated in a single-shot fashion, but this method did not allow the operator to control the open time precisely, since the open time of the valve corresponded to the amount of time the single-shot button was depressed. When the solenoid was being governed by the control box, it had specific operating ranges. The pulsing frequency of the solenoid could be varied between 0 and 120 Hz, while the open time could be varied from 0.16 ms up to its maximum (a few seconds). The frequency of pulsing was controlled by the pulse generator and the open time of the solenoid was varied by a potentiometer in the control box circuit. The rising edge of the pulse generator square wave triggered the solenoid to open, in addition to triggering the MCA, which was used to collect all of the data (i.e., AA, AE, and MS signals) for these experiments. The MCA was used exclusively since only one mass could be monitored at a time to observe the individual time-resolved characteristics.

The water reservoir (a 0.75" glass bulb, as described in Chapter 3) was attached to the injection valve by a Cajon connector; water vapor residing above the liquid was pulsed into the ion source. In order to make the amount of water being injected with each pulse consistent, the space above the liquid water was
evacuated, either with an attached roughing pump or through the injection valve into the ion source. The former method was most often used in order to keep the ion source contamination to a minimum. Without this process, the first few injection pulses will contain a large quantity of air with the water vapor. This process was repeated after the system had remained idle for an extended period of time, in case there were any air leaks into the water reservoir. The system was considered to be providing a consistent amount of water vapor when the ion signal profile changes were the same from pulse-to-pulse, within experimental error.

Before using the pulsed injection valve, studies were performed by introducing a short burst of water vapor simply by opening the shut-off valve, shown in Figure 41, for a short period of time. However, this method of water vapor introduction was found to be irreproducible. Figure 62A shows the titanium ion signal measured when using this method. It is clear that this method is not sufficient for measuring reproducible changes in the plasma as water vapor is introduced. Not only is the magnitude of the signal loss different for each pulse, but these varying amounts of water vapor introduction lead to different recovery times and signal profile behavior. The solenoid system was designed to pulse small and controllable amounts of water vapor into the mass spectrometer ion source. Figure 62B shows the reproducibility of the pulsed solenoid introduction valve method as compared to manually opening the needle valve assembly. The signal fluctuations upon introducing the water in a 2 min cycle are shown to be very reproducible with the characteristics of each pulsed signal being the same.
Figure 62 Comparison of pulsed water vapor introduction methods.  A) Opening shut off valve by hand; B) Use of the solenoid valve.
The open times that were used in the experiments described in this chapter generally varied between 5 and 100 ms. The time that was used usually depended on the observed effects for a given cathode. Shorter open times were used for an element such as copper, which does not readily remove water vapor by gas-phase reactions, and longer times were used for reactive elements such as titanium.

Results and Discussion
Transient Behavior of Matrix Species

This section will discuss the results from the studies of pulsed water vapor introduction while monitoring the ion signal response of a variety of matrices. Some of the differences that are observed were anticipated because of the results reported in Chapter 3. The titanium was expected to suffer the least adverse effects from the pulsed introduction of water vapor due to its gettering ability. The reactions of titanium with water in the gas phase should facilitate its fast recovery to an equilibrium condition and minimize any possible surface contamination. On the other hand, some cathodes that might suffer from water oxidation on their surfaces due to their minimal gettering ability, will be affected the most.

Information on the ion-molecule reactions involving metallic element ions has been scarce until recently. A large volume of work has been published in the past decade that shows the periodic trends of the reactivities of the first row transition metals. Although none of this work has involved the reactions of metal ions with water, some comparisons may be made to the trends observed using reactions with other species. Many different aspects were found to control the
efficiency of the reactions of the first row transition metals, but the general trend that was observed was metal ions on the left side of the period were more reactive than the metal ions on the right. This may be due to a variety of factors, such as the reaction cross section for metal ions (which generally decreases across the period) [123,124] and the electronic state of the metal ion [125,126,127]. In most cases, the reactions shown in these references (M$^+$ with H$_2$, D$_2$, O$_2$, and N$_2$O) were more efficient with elements on the left side of the fourth period and decreased across the period. This is in agreement with observations made in the glow discharge using titanium, iron, and copper ions in reactions with water vapor.

Titanium. Since titanium is a gettering material, it can exhibit gas-phase reactions that will speed the cleaning of the discharge environment. However, the surface of the cathode can become contaminated with water and oxide species if the amount of water in the plasma is enough to overcome the gettering abilities of the element. In the experiments presented here, the amount of water that is introduced is quite small in comparison to those discussed in Chapter 3. Therefore, it would be expected that the effects of pulsed injection would be minimal when using the titanium cathode, because the pulse of incoming water may be consumed in the gas-phase reactions before it is allowed to affect the surface greatly.

Figure 63A shows the titanium ion signal response to a 30 ms pulse of water vapor into the GDMS ion source. The signal recovery is very quick for this cathode material, in comparison to the other cathodes that will be discussed
Figure 63  Ion signal profiles obtained with a 30 ms pulse of water vapor.  A) Titanium ion signal; B) Titanium oxide ion signal.
below. The slope of the recovery is sharp, similar to that shown in Chapter 3. Since the ion signal is only suppressed for a short time, it is believed that the water pulse is short enough not to affect the surface but only affect gas-phase reactions. For a gettering material such as titanium, these gas-phase reactions will include the formation of metal-oxide species. This is shown in Figure 63B, where the formation of the titanium oxide ion signal corresponds to the decrease in the titanium ion signal. When longer open times or faster repetition rates are used, the ion signal profiles will not reach their plateau value, indicating that the system is not recovering between pulses. At this point, the amount of water introduced into the system has overcome the ability of the titanium to getter-clean the discharge environment and the surface interactions are becoming more predominant.

**Copper.** As mentioned in Chapter 3, copper is a species that will often have water peaks in its mass spectrum unless ultra high purity sputtering gases are used. This is due to the lack of gettering reactions by copper to help clean up the discharge environment. Also, since the reactivity of copper is considered lower than the other elements used in these studies, its recovery to a "clean" environment will take longer.

Figure 64 shows both the copper ion signal and the copper emission signal ($\lambda = 324.75$ nm) upon adding a 5 ms pulse of water vapor to the mass spectrometer ion source. The shape of the copper recovery should be noted and compared to the results shown in the last chapter. In both cases the recovery is fairly slow compared to a species like titanium. Note that the slope of the copper
Signal profiles obtained from a copper pin when a 5 ms pulse of water vapor was introduced. A) Copper emission; B) Copper ion signal.
signal as it recovers from the water vapor introduction is not as great as for titanium, even with the reduced open time for the pulsed solenoid valve. These results are in agreement with the previous results discussed in Chapter 3.

Iron. Iron was studied also and should exhibit a behavior somewhere between that of copper and titanium since it lies in the middle of the first row transition metals. Figure 65 shows the behavior of the iron signal from a stainless steel pin with the introduction of a 30 ms pulse of water vapor. The number of pulses in this figure is increased to demonstrate the reproducibility of the pulsing valve. The water valve was pulsed 10 times, as shown in this figure, and the integrated ion signal counts over the two minute period was calculated. For this particular data the signal intensity was $1.0 \times 10^7 \pm 1.65\%$. This is a typical standard deviation over ten pulses for the cathode materials under study. The behavior of the iron signal profiles also shows a quick recovery, as did the titanium. However, this recovery time is not quite as rapid as for titanium. This is difficult to see in this figure since there are ten pulses shown. With the iron cathode there is a sharp transition back to the plateau value as was illustrated in Chapter 3.

The reproducibility of the results of some of the ion signal profiles that were studied while sputtering a stainless steel pin are illustrated in Table IX. The reproducibility was demonstrated to be best for the matrix ion, its oxide ion, and the argon species. Gaseous contaminant species showed a larger deviation with the species at m/z 29 ($N_2H^+$ and $COH^+$) being the worst.
Iron ion signal profiles obtained from a stainless steel pin when a 30 ms pulse of water vapor was introduced.
Table IX. Reproducibility of the Pulsed Solenoid Valve on the Detected Ion Signal Intensities with a Stainless Steel Cathode.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Signal Intensity (counts)</th>
<th>%RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{56}\text{Fe}^+$</td>
<td>$1.0 \times 10^7$</td>
<td>1.65</td>
</tr>
<tr>
<td>$\text{H}_3^+$</td>
<td>$8.9 \times 10^6$</td>
<td>3.00</td>
</tr>
<tr>
<td>$\text{OH}^+$</td>
<td>$8.5 \times 10^5$</td>
<td>9.23</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}^+$</td>
<td>$6.0 \times 10^6$</td>
<td>7.44</td>
</tr>
<tr>
<td>$\text{H}_3\text{O}^+$</td>
<td>$3.3 \times 10^6$</td>
<td>8.34</td>
</tr>
<tr>
<td>$\text{Ar}^{2+}$</td>
<td>$3.3 \times 10^6$</td>
<td>3.85</td>
</tr>
<tr>
<td>$\text{CO}^+, \text{N}_2\text{H}^+$</td>
<td>$4.1 \times 10^5$</td>
<td>25.31</td>
</tr>
<tr>
<td>$\text{ArH}^+$</td>
<td>$4.1 \times 10^6$</td>
<td>2.82</td>
</tr>
<tr>
<td>$\text{FeO}^+$</td>
<td>$2.1 \times 10^5$</td>
<td>3.11</td>
</tr>
</tbody>
</table>
Zinc. Zinc is another species that is of interest in glow discharge studies. Since it is a relatively soft material with a low melting point, it requires a lower discharge voltage than some of the other materials. This makes it more susceptible to gaseous contaminants since these species are more dominant when the glow discharge is operated at a reduced voltage. At these lower voltages, the "cleaning" processes of the discharge are not as efficient as they might be if the cathode were operated at a higher voltage. It has been previously shown, with a stainless steel pin, that as the discharge voltage is increased, the ion signal intensities of water vapor and other contaminant gaseous species will decrease [128]. For comparison, the zinc cathode was operated at 1000 V and 3.2 mA, while the stainless steel cathode could be operated at 1250 V and 5.0 mA. These detrimental factors are illustrated in Table X, which lists the reproducibility of some of the ion signals monitored while using the zinc cathode. The standard deviations when using the zinc pin are generally higher than for the stainless steel pin. Even the signal from the zinc cathode itself shows a quite large %RSD. The zinc oxide signal has a large %RSD as well, but this is somewhat attributable to the conditions that must be used to monitor this species. The highest zinc oxide signal will occur at m/z 80, which is also where the argon dimer is detected. For this reason the zinc oxide signal at m/z 82 was used. This was formed with the isotope $^{60}$Zn and oxygen. Since this isotope is less abundant (about 50 % of the $^{64}$Zn isotope), the detector must be operated at a higher gain and subsequently more noise may be introduced in the detected signal.
Table X. Reproducibility of the Pulsed Solenoid Valve on the Detected Ion Signal Intensities with a Zinc Cathode.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Signal Intensity (counts)</th>
<th>%RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{64}\text{Zn}^+$</td>
<td>$3.9 \times 10^6$</td>
<td>8.77</td>
</tr>
<tr>
<td>$\text{H}_3^+$</td>
<td>$9.6 \times 10^6$</td>
<td>2.17</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}^+$</td>
<td>$5.8 \times 10^5$</td>
<td>9.32</td>
</tr>
<tr>
<td>$\text{H}_3\text{O}^+$</td>
<td>$1.2 \times 10^6$</td>
<td>22.01</td>
</tr>
<tr>
<td>$\text{Ar}^{2+}$</td>
<td>constant decrease</td>
<td>-</td>
</tr>
<tr>
<td>$\text{ArH}^+$</td>
<td>$4.1 \times 10^6$</td>
<td>1.73</td>
</tr>
<tr>
<td>($^{68}\text{ZnO}$)$^+$</td>
<td>$1.1 \times 10^5$</td>
<td>8.12</td>
</tr>
</tbody>
</table>

Note that $^{68}\text{ZnO}^+$ was used, since $^{64}\text{ZnO}^+$ will be interfered by $\text{Ar}_2^+$. 
Effects of Pulsed Water on Other Plasma Species

The experiments that are discussed in this section will demonstrate the effects of the pulsed water on other species that are formed or reside in the glow discharge plasma. The species that were investigated are similar to those reported in Chapter 3 (i.e., water species, argon species, and M-O species).

Water dissociation species. As reported in Chapter 3, the various species formed upon the dissociation of water vapor were observed to increase at the ion signal transition point, while the water vapor species showed a corresponding decrease. In the experiments shown here the plasma environment will not be subjected to the relatively large amount of water vapor that was present with the steady state introduction. It is therefore expected that upon the pulsed introduction of the water vapor into the plasma, the water dissociation species will show an increase as the water is dissociated by the discharge and will then be removed from the plasma environment by reactions or pumping. Figure 66 shows the two prominent water dissociation species that were monitored in these experiments. Figure 66A shows the ion signal behavior of the $H_3^+$ signal when a 30 ms pulse of water was introduced. The cathode being used was a stainless steel pin. The behavior of these species was the same for all the cathodes, only the residence times of the individual ions in the plasma were different. These species were detected longest for copper and shortest for titanium, since the removal may be expected to be faster with a reactive metal versus a more inert metal. Figure 66B shows the ion signal response for $OH^+$. The signal profile and characteristics are very similar to that shown for $H_3^+$. This indicates that upon the
Figure 66  Signal profiles obtained with a 30 ms pulse of water vapor into a stainless steel discharge. A) $H_3^+$ ion signal; B) $OH^+$ ion signal.
pulsed introduction of water, these species begin to immediately dissociate in the discharge.

**Water species.** The water ion signals in the glow discharge plasma (i.e., $\text{H}_2\text{O}^+$ and $\text{H}_3\text{O}^+$) are expected to behave similarly to that described in the previous section, since the same ion molecule reactions are occurring in the plasma. Upon the pulsed addition of the water vapor, the water ion signals should increase with the shifting of the discharge equilibria. The water signal should rise sharply, and since there will be minimal interactions with the cathode surface, the gas-phase reaction processes (i.e., metal-water vapor reactions and water dissociation reactions) should determine the rate at which water vapor is removed. Thus, as previously mentioned, the reaction efficiency would be expected to be greater with titanium than with copper.

Figures 67, 68, and 69 illustrate the relative ion signals from the $\text{H}_2\text{O}^+$ and $\text{H}_3\text{O}^+$ species, as the water is pulsed into the system with titanium, iron, and copper cathodes, respectively. For the titanium and iron profiles the water injection valve was opened for 30 ms, while for the copper data the valve was opened only for 5 ms. It should be noted that the main difference between these three figures is the time required to remove the water species from the plasma. It was observed that the titanium was the best cathode for removing the water from the ion source, followed closely by iron. Even with the reduced solenoid open time for the copper cathode, the water species are present in the plasma for a longer period of time (approximately 45 s, versus 5 - 10 s for the other two cathodes).
Figure 67  Water ion signal profiles obtained with a 30 ms pulse of water vapor into a titanium discharge. A) H$_2$O$^+$ ion signal; B) H$_3$O$^+$ ion signal.
Figure 68  Water ion signal profiles obtained with a 30 ms pulse of water vapor into a stainless steel discharge.  A) $\text{H}_2\text{O}^+$ ion signal; B) $\text{H}_3\text{O}^+$ ion signal.
Figure 69  Water ion signal profiles obtained with a 5 ms pulse of water vapor into a copper discharge. A) H$_2$O$^+$ ion signal; B) H$_3$O$^+$ ion signal.
**Argon species.** The species that were monitored to determine the argon behavior in the plasma were ArH\(^+\) and Ar\(^{2+}\). It was determined from the previous chapter that these two species, along with Ar\(^+\) and Ar\(^{2+}\), show a similar behavior, so only ArH\(^+\) and Ar\(^{2+}\) are illustrated. Also, these species were the largest ion signals obtained for argon containing ions. ArH\(^+\) is larger than Ar\(^+\) in this system due to the plasma conditions that are being used (with the water and subsequent hydrogen contamination, as discussed in Chapter 3). Figure 70A shows the ion signal behavior of ArH\(^+\) as a 30 ms pulse of water was introduced into the discharge having a stainless steel pin cathode. Figure 70B shows the ion signal behavior for Ar\(^{2+}\) under the same conditions. The ion signals show a decrease in intensity upon the addition of the water vapor. This is expected in relation to the plasma reactions that have been previously discussed in Chapter 3. The extent of the detrimental effects that were observed for different cathodes correlated with the amount of time it takes to remove the water vapor from the plasma. As with the other results presented above, copper has the most detrimental effects, while titanium can keep the plasma environment clean.

**Metal-oxide species.** With the introduction of water vapor into the ion source, the plasma environment will become more oxidizing and this can be demonstrated with the observation of the formation of oxide species in the plasma. Figure 63 shows the corresponding production of a titanium oxide ion signal with the reduction in the titanium ion signal. This is direct evidence of the formation of an oxide species with the introduction of water. The loss in titanium may be attributed to losses in sputtering, ionization, and an overall loss of some
Figure 70  Argon species ion signal profiles obtained with a 30 ms pulse of water vapor into a stainless steel discharge. A) ArH$^+$ ion signal; B) Ar$^{2+}$ ion signal.
titanium that is reacting with the water and its dissociation species in the plasma. Figures 63A and 63B should not be compared directly, since the gain on the detector was increased to obtain the titanium oxide ion signal. Therefore, it should be noted that the signal intensity of the oxide species compared to the metal is orders of magnitude smaller. All matrices were found to form a metal-oxide species in the discharge upon the injection of water vapor. The amount of oxide formation that occurred in the plasma can be correlated with the M-O bond strength. For the species under investigation, the M-O ion signal intensity followed the decreasing trend: TiO$^+$ > FeO$^+$ > CuO$^+$.

**Use of Liquid Nitrogen Cooling**

The liquid nitrogen cooling coil was also used in some of these experiments. This method was used to see if the water vapor that was injected in the gas phase will deposit on the coil before interfering with the plasma interactions. Figure 71A shows the water ion signal profile for a new copper pin, at a time when the plasma has not yet become "clean." Under these plasma conditions, the ion signal profile for the water species does not reach a zero intensity level between pulses. After this profile was obtained, liquid nitrogen was added to the cryogenic coil and the ion signal profile for H$_2$O was observed, as shown in Figure 71B. Even with liquid nitrogen cooling, the copper discharge will still have a larger water ion signal than that obtained with either iron or titanium cathodes.

Figure 72 shows the effects of liquid nitrogen on the copper ion signal profile upon the introduction of a 5 ms pulse of water vapor when the liquid
Figure 71  Water ($H_2O^+$) ion signal profiles obtained from a copper pin when a 5 ms pulse of water vapor was introduced.  A) without liquid nitrogen cooling; B) with liquid nitrogen cooling.
Figure 72  Copper ion signal profile obtained when a 5 ms pulse of water vapor was introduced and liquid nitrogen cooling was used.
nitrogen coil is in the ion source. Figure 64B shows a typical signal profile that was obtained of the sputtered copper ions under normal conditions. The data presented in Figure 72 were obtained a few minutes after adding the liquid nitrogen to the cooling coil. The differences in the recovery time of the ion signal back to its original equilibrium state can be easily seen. The behavior of the copper ion signal profile with liquid nitrogen is very similar to the behavior of the titanium ion signal shown in Figure 63A. Although the recovery time is not quite as fast, the sharp transition back to an equilibrium state is similar. From this experiment it may be concluded that the liquid nitrogen coil will remove much of the water vapor from the gas phase and the inert metal ion signal will not be affected as much.

As mentioned in Chapter 3, the time that the liquid nitrogen coil may be used effectively is limited. It was observed that after pulsing the solenoid for a period of about two hours, the area of the coil facing the injector would become covered with ice crystals. When this condition occurs, the coil has to be allowed to warm up and the system must pump away the excess water. However, with the limited amount of water vapor that is allowed into the source under these experimental conditions, the useful time of the cryogenic coil is enhanced compared to the experiments described in Chapter 3. Under typical experimental conditions, the useful time for liquid nitrogen cooling should be even longer since there is no external water vapor being added to the source. In these experiments the water vapor will come from sample introduction, outgassing from the chamber walls, and the sample itself.
Effects of Pulsed Water on the Atomic Population

As discussed earlier in Chapter 3, it is advantageous to monitor the atomic population in these systems to observe the effects that the addition of water vapor will have on the neutral and excited atomic populations in the plasma. The experimental setup used was discussed in Chapter 1 and all of these experiments were performed on the Extrel instrument.

Atomic absorption and atomic emission measurements were conducted on the two most prevalent atoms of interest in the glow discharge plasma: the sputtered (cathode) atoms and the argon metastable atoms. The measurement of the absorption or emission of the sputtered species will give an indication of how the water vapor is affecting the sputtering processes in the glow discharge. As mentioned earlier, it is expected that the addition of water vapor will reduce the sputtering since some of the water dissociation products (i.e., H\textsuperscript{+}), which have a low mass and a high mobility, will contribute a large amount to the discharge current but will do little to aid in sputtering. This will be seen experimentally with a decrease in the absorbance or emission signal obtained from the species upon the introduction of water vapor. The absorbance or emission of the argon metastable atoms will give a direct indication of how the sputtered species ionization is being affected in the plasma. A decrease in the argon metastable absorbance or emission value will indicate that either the metastables are being quenched or their formation is reduced. This will result in a decrease in Penning ionization, which is primarily responsible for the ionization of sputtered species in the plasma.
Analyte atoms

The AA and AE measurements on the analyte atoms in the plasma give an indication of the effect that the water vapor introduction has on the sputtering process. As mentioned previously, the sputtering will be reduced as the water content in the plasma is increased. Since either AA or AE measurements will give an indication of the atomic population of the sputtered species in the plasma, it is not typically crucial to these studies which measurement is chosen. However, if a cathode that is being measured has a high sputter yield (such as the copper), it is advantageous to use emission measurements. This is because the absorbance for copper atoms in the plasma is very high. Thus, when small pulses of water are introduced into the system, the absorbance measurements will not change greatly. This would also be true if the sputtered atoms are very efficient absorbers, where even a small amount of atoms will result in a large absorbance value.

Figure 73 shows the absorbance and emission signal profiles obtained for the titanium when a 30 ms pulse of water was allowed into the ion source. As expected, these signals are reduced when water vapor is pulsed into the plasma, indicating that the sputtering may be reduced or the atoms may be tied up in the oxide form during this time. The profile shown in Figure 73A shows a short lived loss in absorbance signal. The signal reaches its plateau level again after about 15 s. However, the titanium emission signal (see Figure 73B) shows a decrease in signal that does not regain its plateau value for about 30 seconds. The formation of excited atoms lags behind the ground state species in reaching their
Figure 73 Signal profiles obtained with a 30 ms pulse of water vapor into a titanium discharge. A) Ti absorbance; B) Ti emission.
equilibrium value. This may be a result of collisions of the excited species with water vapor in the ion source that does not allow the excited species population to regain its equilibrium value until the water vapor is removed.

**Argon metastables**

The signal behavior of the argon metastable atomic population is shown in Figure 74. It is important to monitor the argon metastable population since this determines the extent of the Penning ionization in the glow discharge plasma. The behavior of the argon metastable profile is very similar to that shown for the titanium atoms. Upon the introduction of the water vapor into the ion source, the argon metastable population is reduced due to the efficient transfer of energy from the argon metastable to the water molecule [86]. Figure 74A shows the argon metastable absorbance data that give an indication of the neutral argon metastable species population in the plasma. This measurement is the absorbance occurring at \( \lambda = 811.5 \) nm, which is the transition \( ^3P_2 \rightarrow ^3D_3 \). Figure 74B shows emission at the same atomic line. This is a measurement of the emission intensity of transitions terminating at a metastable level, which may be used to estimate the population of argon metastable species. Emission measurements at this line may produce errors in the absolute number densities for the metastable population, because all transitions are not accounted for (e.g., direct electron excitation and possible electron-ion recombination) [129]. However, generalities on plasma effects may be made using this argon emission line. Both graphs show a similar profile and time of recovery. However, the
Figure 74  Signal profiles obtained with a 30 ms pulse of water vapor into a titanium discharge. A) Ar* absorbance; B) Ar* emission.
argon metastable emission is quenched to a greater extent that the argon metastable absorbance.

The results presented in these sections illustrate that the effects of water vapor introduction into the glow discharge are two-fold. Since the titanium emission is reduced, there must be a loss of sputtering in the plasma. Also, since the argon metastable population is reduced, the ionization in the plasma is also decreased.

**Power Supply Operation**

The behavior of the species under investigation was further explored to be sure that the signal changes being observed were real and not just an anomaly of the power being supplied to the cathode. The majority of the studies were performed with the power supply being operated in the constant voltage mode. Upon each pulse, a short-lived decrease in the discharge current was also observed. This decrease in current could possibly be a factor in the decrease of ion signal that was detected. Recall, that when water was added to the ion source as described in Chapter 3, there was a correlating decrease in the discharge current and the discharge current was found to be inversely proportional to the water concentration in the plasma. However, in those experiments it was noted that the ion signals did not follow the current characteristics exactly. For example, many abrupt changes were observed to occur when the ion signals went through their "transition points." At this particular point in the experiments, there was not a corresponding quick change in the
discharge current. Rather, the current slowly returned to its typical value as the water was removed.

The purpose of these experiments is to determine if these changes in the discharge current during constant voltage operation has a more dominant effect here, since the changes in current and ion signal both occur in a short time frame. While running the discharge in both constant current and constant voltage mode, the ion and neutral atomic signal characteristics were observed as before using MS, AA, and AE.

**Constant voltage**

When running the discharge with a constant voltage power supply there will be a constant energy of the bombarding species on the cathode surface, but as the current changes the number of ions striking the cathode will change. Figure 75 shows the current profile that was obtained while running the glow discharge in the constant voltage mode. From these observations, it may be thought that the decrease in ion signal is a result of the change in discharge current.

**Constant current**

When operating the discharge in the constant current mode, the number of ions impinging onto the cathode surface will remain the same. However, the energy of the ions arriving at the surface will change as the voltage changes. Figure 76 shows the response of the discharge voltage as the water is pulsed into the system. From this observation, one might expect an increase in the ion signals previously shown.
Figure 75. Discharge current profile obtained from a titanium pin operating at a constant voltage of 1250 V when a 30 ms pulse of water vapor was introduced.
Figure 76  Discharge voltage profile obtained from a titanium pin operating at a constant current of 4.0 mA when a 30 ms pulse of water vapor was introduced.
The ion signal profiles obtained under these different operating conditions show a very similar behavior. Figure 77 shows the titanium ion signal obtained while operating the discharge in both the constant voltage and constant current mode. Upon initial observation of these profiles, it was determined that the power supply operation was not affecting the ion signal profiles that were being detected. The major difference between these two operating parameters is that in constant current mode, the recovery time appears to be slightly faster. This is most likely due to the increase in voltage that occurs when the water is pulsed into the system. A higher voltage will increase the energy of the plasma and will allow the plasma environment to "clean up" faster, as mentioned previously. Therefore, the changes that are being observed upon the pulsed injection of water vapor into the ion source are not attributable to the differences in the power supply operation, even though there are changes in the voltage and current as the other parameter is held constant. Similar profiles were obtained with the sputtered species and argon metastable atoms in the plasma. The effects of both operation modes were similar, only the recovery time was slightly enhanced when running in the constant current mode.

Conclusions

This chapter has described additional experiments that have been performed to explore the effects of water vapor on the glow discharge plasma processes. The results that were obtained are in agreement with those observed in Chapter 3. The water introduction method described in this chapter allowed the determination of the processes occurring primarily in the gas phase of the
Figure 77  Titanium ion signal profiles obtained with a 30 ms pulse of water vapor into a titanium discharge. A) Constant voltage operation; B) Constant current operation.
glow discharge, since the surface-water interactions are kept to a minimum with
the short pulse times used. As expected, the titanium is the least affected since
it exhibits efficient gas-phase reactions that will keep the water effects to a
minimum. The water dissociation species in the plasma showed an increase
upon the introduction of the water vapor, since the discharge environment will
promote this process. These species then decreased in intensity as they were
pumped and reacted out of the system. The pulsed water showed a detrimental
effect on the argon species in the plasma as well, very similar to that shown in
Chapter 3. The water species ion signals were shown to increase upon the
pulsed introduction of water vapor and the recovery time for the system to reach
equilibrium was different for each cathode. The titanium cathode removed the
water and its effects the fastest, while the copper cathode took the longest. The
effects on sputtering were monitored by observing the changes in the atomic
absorption and atomic emission of the analyte species. All of the cathodes under
study showed a 40 - 60 % decrease in the analyte atomic population upon the
introduction of the water vapor. Also the effects on Penning ionization were
observed by the decrease in the argon metastable atomic population. These
experiments show that even a small introduction of water vapor into a glow
discharge environment can have effects that last from a few seconds to about one
minute.
CHAPTER 5
FINAL REMARKS AND FUTURE DIRECTIONS

The experiments performed for this dissertation were a progression from the introduction of aqueous solutions into the GDMS ion source to studies of water vapor effects. Since the aqueous solution method was limited by the introduction of contaminants with each sample, it was of interest to study the water vapor effects on the fundamental processes and analytical utilities of the glow discharge. Water vapor problems are difficult to avoid since the analysis must be performed quickly after initiating the glow discharge to avoid sample loss. With a normal pin cathode, it often takes as much as 10 - 15 min to obtain a stable discharge. Therefore, if the cathode is brought in and out of the ion source in the same manner described earlier for the solution analysis and data were collected in the first minute of sputtering, similar levels of standard deviations might be obtained. Thus, the inherent operation of the glow discharge limits this type of sample introduction, where data collection starting immediately after initiating the discharge is required.

Final Remarks

Aqueous Solution Samples

Electrothermal vaporization has been used to analyze solution samples quickly in a GDMS system and its characteristics were shown to be similar to those of other GDMS systems. The sampling sequence is an important part of
the method development, since sample dryness and sampling sequence timing need to be accurate. The amount of sputtering loss before initiation of the electrothermal filament should be minimized, but the initial sputtering time should be sufficient to provide a stable discharge. This was obtained in a minimum time of 5 s, which does not result in a large loss of ion signal (a few tenths of a percent of the total). The ion transmission from both an auxiliary cathode and the filament itself was dependent on the parameters used. Maximum ion signals were obtained with a constant voltage discharge and the maximum filament current, so these parameters were used for the majority of the studies. The method showed linearity in the limited concentration range studied for these experiments, and the optimum operating pressure was found to be about 1.2 Torr argon, which is consistent with that used for a typical glow discharge application. A major difference that was observed with this source is the cathode-to-ion exit orifice distance that produces the maximum ion signal. For the electrothermal source, the maximum signal was observed with the filament 3.5 mm from the ion exit orifice. This difference may be a result of larger electron production from the filament than observed for a typical glow discharge, or the atoms in the plasma may be at different energy levels than those of the typical discharge. The positioning of the sample on the filament is a critical parameter as well, with the maximum ion signal obtained when the sample is applied at the end of the filament nearest the ion exit orifice. The ETV/GD method shows no significant memory effects when a blank sample is used, which is important since many analyses of this type suffer from memory effects. Multi-element samples may be
analyzed to some extent. Only binary elements were demonstrated in the data presented here, since the elements must be in a narrow mass range. Improvements would be expected with a fast scanning system and the use of internal standards to improve quantitation. Binary samples were separated by ramping the filament current, but this method requires elements that are far apart in their atomization temperatures unless the power supply is computer controlled. Internal and external ETV introduction schemes were used and compared. The internal method is preferred, due to its simplicity and better sensitivity. However, internal ETV introduction suffers from higher relative standard deviations and erosion of the filament material. The overall inconsistencies of this technique have been attributed to the continual introduction of contaminant air and water vapor with each subsequent sample.

**Effects of Water Vapor on GDMS**

Water vapor effects in the plasma can occur to various degrees depending upon the cathode material that is used, the purity of the discharge gas, and the integrity of the vacuum system. The reduction in ion signal, observed with the mass spectrometer, is most likely due to a combination of inefficient sputtering, oxidation of the sample surface, loss of analyte atoms through gas phase reactions, and quenching of argon metastable atoms that are responsible for ionization. Many surface and gas-phase reactions are occurring in the ion source as the water vapor content is changed in the plasma. It was found that during the initial period, after the steady state introduction of water vapor was suspended, the greatest detrimental effects were attributed to the surface interactions of the
cathode. Elements with a greater reactivity toward water vapor in the ion source form a more tenacious oxide layer and result in a longer period of time before an ion signal is detected. Once sputtering is initiated and the surface begins to be cleaned, then gas phase reactions seem to dominate. In this realm, the cathode materials that are more active toward water vapor species will react with them and remove them from the system, resulting in a cleaner spectrum. Water dissociation products and hydrogenated species (i.e., N$_2$H$^+$ and COH$^+$) show similar effects and are considered to be in an interactive equilibrium with one another. The same is true for the various argon species in the plasma that exhibit very similar behavior toward the water vapor content in the plasma. The use of a liquid nitrogen coil was demonstrated to alleviate the effects of added water vapor by freezing out the contaminants and results in a mass spectrum that is dominated by the elemental ion signals.

Pulsed introduction of water vapor was studied to observe the time-dependent effects a small short-lived water pulse would have on the plasma processes. With this introduction device, the amount of water vapor introduced into the plasma can be limited and should not affect the surface of the cathode. Gas-phase reactions of the cathode material and the sputtering processes should not allow a surface oxide layer to form as long as the solenoid open time is kept short (this time will vary with the cathode material). The gettering elements, such as titanium, were found to be affected the least while water vapor had the greatest detrimental effects on copper. Upon pulsing water vapor into the source, the matrix species and the argon species were reduced, while the metal-oxide
species, water species, and water dissociation products ion intensities were increased for a short period of time. The operation of the discharge in the constant current and constant voltage modes were compared and found to give similar results. However, when operating at a constant current, the return to an equilibrium condition after water introduction is enhanced due to the increase in discharge voltage.

The effects observed in these experiments will become important in the analysis of an alloy or other real-world sample that contains a variety of elements. Since ion signals of different elements are affected to different degrees in the presence of water, calibration data for quantitative analysis (e.g., RSF values) that are obtained at unknowingly different water concentrations in the plasma can no longer be reliably used. Therefore, it is especially crucial that the water content in a glow discharge ion source be controlled to a constant and minimal level for quantitative analysis.

Future Directions

Aqueous Solution Samples

Aqueous solution samples in the glow discharge suffer most from the introduction of water vapor into the ion source. If the time required to analyze a solution sample were not ideally in a short time frame, the results could most likely be improved. Future studies for the analysis of solutions in GDMS will probably involve mixing the sample with a powder and drying the mixture, followed by pressing the sample into a pin or disk for analysis, or the application of the solution to a cathode that is dried and subsequently analyzed. These two
techniques do not give the improvement in sensitivity observed with the current ETV/GD method, but will result in a more reproducible analysis since the drying of the sample is assured. If the surface deposition on the cathode is used, then the analysis must occur in the early times of discharge sputtering and might result in deviations similar to those seen for the ETV/GD technique. Using the mixing method results in a long lived signal that may be stabilized over the first few minutes of sputtering and give more reproducible results.

As for the ETV/GD method, some improvements in the experimental method are needed. First, there is the need to use internal standards for quantitative analyses so that any changes in the plasma conditions from run to run may be corrected for. However, in the light of the studies conducted with the water vapor, the internal standard must be ideally chosen to interact with water and other contaminants in a similar manner as the analyte. Second, mass spectral scanning needs to be faster. If the internal standards method is to be useful or multi-element species are to be analyzed, then repetitive rapid scanning over a large mass range is needed.

Effects of Water Vapor on GDMS

Water vapor and its reactions in the plasma remain an intriguing focus of glow discharge research, since this contaminant species is always present to some extent in the discharge ion source. Almost any analysis will require some period of "pre-sputtering" to remove the water contaminants from the sample surface and the ion source. This is of particular importance for powdered samples that are pressed into a cathode disk, since water is often occluded into
the sample itself and will migrate out of the cathode over the experiment time. Many of the reactions that were illustrated in this dissertation are of interest in fully understanding the mechanisms of water interactions in the glow discharge plasma. To understand these phenomena better, the introduction of isotopically labeled water would be of interest. Using both H$_2^{18}$O and D$_2$O would give further insight into the plasma processes and the dissociation of water vapor species in the glow discharge.
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BIOGRAPHICAL SKETCH

Philip Ratliff completed his Bachelor of Arts degree in chemistry at East Tennessee State University in May 1987. In the fall of that year, his graduate career began at the University of Virginia under the direction of Dr. Willard W. Harrison. With the relocation of Dr. Harrison's research group, he transferred to the Chemistry Department at the University of Florida in January 1989. He completed his graduate studies with a Doctor of Philosophy in August, 1992.
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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This dissertation was presented to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 1992

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