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PROGRESS REPORT

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THE GLOW DISCHARGE AS AN ATOMIZATION AND IONIZATION DEVICE

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PROGRESS REPORT

This report summarizes the research activities in our laboratory over the past 36 months during the Award Period. In keeping with instructions from DOE (DEAS05-80ER 10635, DEFG05-88ER 13885, DEFG05-89ER 14018), we include here only what we feel are the most important developments, and these are summarized to provide a brief overview of our progress. More detailed descriptions of our work are available in the reprints and preprints that accompany this research proposal.

All of our projects involve the glow discharge source as our basic research focus. Our primary effort is glow discharge mass spectrometry, but we frequently use complementary procedures such as atomic absorption and atomic emission in the glow discharge to obtain useful information about plasma processes. Our overall goal is to gain a better understanding of the glow discharge and to bring it to bear on real analytical problems.

1. Collisional Dissociation in GDMS

The principal analytical difficulty encountered in elemental mass spectrometry is the presence of isobaric interferences, i.e., polyatomic ions having the same nominal mass-to-charge ratio, m/z, as monoatomic analyte ions. The focus of this work is the identification of those polyatomic ions that are the source of spectral interferences in GDMS and their reduction or elimination.

The ability to sample solid materials, both conductive and non-conductive, in their native state is afforded readily by the cathodic sputtering process inherent to glow discharge operation. Unfortunately, the collision-rich plasma of the glow discharge provides a convenient medium for the production of polyatomic ions. Vacuum system impurities and sputtered polyatomic species present in the plasma are subject to ionization in the same manner as monoatomic species, principally through collisions with metastable rare-gas atoms (Penning ionization) and energetic electrons (electron impact ionization). Additionally, collisions between two or more monoatomic species in the plasma can lead to polyatomic ion formation through associative ionization or three-body processes. The presence of polyatomic ions should not be taken as an indication of poor performance on the part of GDMS with regard to trace element analysis. Rather, it is a fact that must be considered when conducting an analysis with any elemental mass spectrometry technique. Some investigators have indicated that cooling of the discharge source to liquid N_2 temperatures reduces discharge gas impurities, but will not affect the population of species such as metal dimers or metal argides. These "native" polyatomic species have been the focus of on-going research in this group. These studies involve the reduction of interfering species through collision-induced dissociation using tandem mass spectrometry techniques. This permits the identification of polyatomic ion composition using daughter and neutral loss spectra

and allow prediction of interfered m/z with parent spectra.

A standard triple-quadrupole mass spectrometry system was modified by replacing the standard EI/CI ion source with a glow discharge ion source. The GD was operated with 0.8 Torr Ar fill gas at a constant voltage of 1.2 kV. Sample cathodes were either 1.5 mm diameter rods machined from Standard Reference Materials or 10 mm lengths of high purity metal wire 1-2 mm in diameter. The central quadrupole, Q2, of the mass spectrometer is enclosed in a bent cylindrical chamber that can be pressurized to effect collision-induced dissociation (CID). This RF-only quadrupole is 183 mm long and of a non-linear geometry, bent in the center to an angle of 9°. The non-linear nature of this assembly serves to shield the ion detection region from energetic neutral species that emanate from the GD ion source. Ions are detected by a conversion dynode operated at 19 kV followed by a continuous dynode, Channeltron type, secondary electron multiplier.

Initial studies on the glow discharge system showed that the dimensions of the discharge chamber were limited by spatial constraints in the source region of the mass spectrometer. As a result, the ratio of the sample matrix to discharge gas ions is smaller than expected. Ideally, the mass spectrum will have spectral contributions from discharge gas ions that have less intensity than that of sample matrix ions. Under identical operating conditions, but with a 3.6 mTorr pressure of Ar in the collision cell, a GD mass spectrum was obtained with a greatly reduced contribution from discharge gas ions as compared to the sample matrix ions. The change in spectral appearance is the result of resonant charge exchange between the Ar ions emitted from the source and Ar gas employed as the CID target gas.

When CID is employed, a main concern is the loss of signal due to the scattering of analyte ions. Although charge exchange has been proposed to decrease the population of analyte ions significantly, it should be noted that the difference between the ionization potentials of most elements and argon results in a significant energy barrier to charge exchange between those elemental ions and the Ar collision gas. In general, the binding energy of the polyatomic species under study requires less than 5 eV center-of-mass collision energy for dissociation, thus limiting the number of monoatomic ions lost from charge exchange with the collision gas. The effect of collision cell pressure on the observed sensitivity of analytical species was studied with a laboratory collision energy of 100 V to observe charge exchange induced losses. The effect of increased scattering at higher pressures limits the sensitivity at 4.2 mTorr to about 1% of the maximum sensitivity observed at 0 mTorr.

The analytical utility of CID as a method for reducing the spectral contribution of polyatomic ions is demonstrated in the analysis of trace Mo in an NIST 1265a low alloy steel. The study concerns the removal of $FeAr^+$ ions that interfere with Mo^+ ions in the mass spectra. The GD was operated at 1.2 kV in 1 Torr Ar. The

total Mo concentration in the sample is 50 ppm. The ^{96}Mo isotope is present at 8.3 ppm and the ^{100}Mo is present at 4.8 ppm. The GDMS spectrum in Figure 1A was obtained in the absence of collision gas. The observed isotope pattern matched that of Fe rather than Mo due to the dominant contribution of $FeAr^+$. Keeping all conditions identical except for adding Ar to the collision cell at 3.61 mTorr resulted in the spectrum shown in Figure 1B. Comparison of this spectrum with the bar graph showing the isotope pattern of Mo in Figure 1C shows very little contribution from $FeAr^+$. At most this species contributes a signal equivalent to 1 ppm at mass 96. In the previous spectrum, this contribution was calculated to be on the order of 2500 ppm.

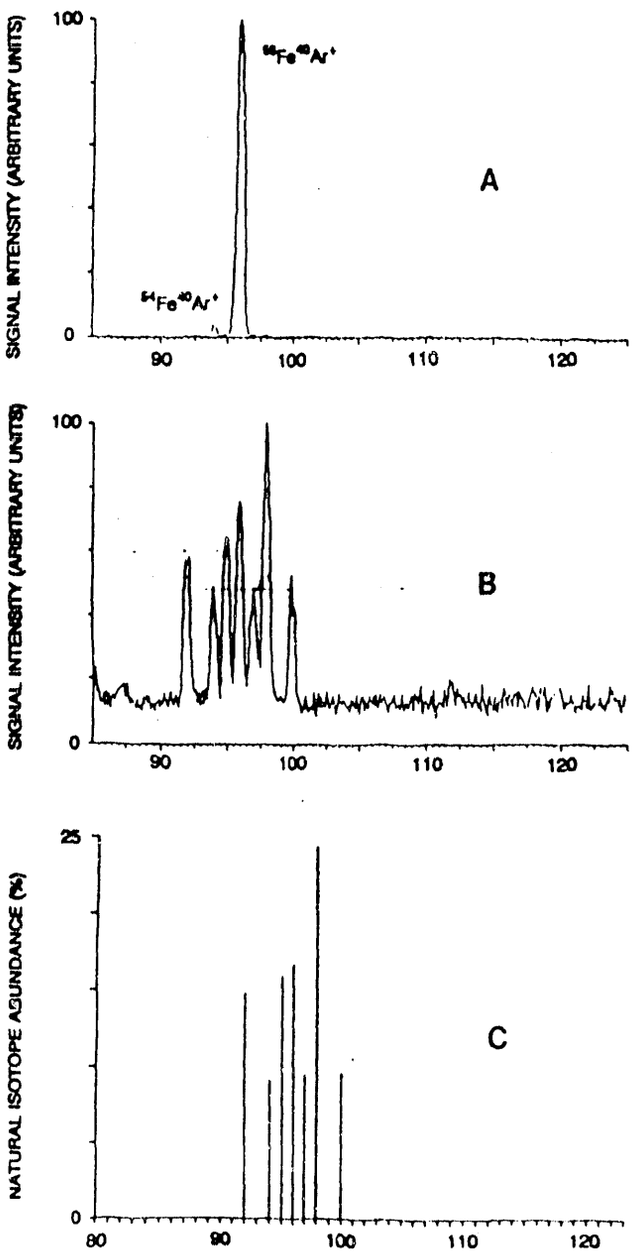

Figure 1

The most common use of MS/MS in organic work involves the acquisition of daughter spectra for particular m/z parent ions under various conditions. In the traditional daughter mode, ions of a selected mass are transmitted by the first quadrupole, Q1, undergo dissociation in Q2, and the resulting fragment ions are analyzed by the third quadrupole, Q3. In trace element analysis, daughter spectra can indicate the presence or absence of molecular ions at a particular m/z of interest. It is assumed that the ^{100}Mo isotope is moderately interference free in the GDMS analysis of stainless steel. This was tested using a daughter spectrum of the m/z=100 ions obtained for an NIST 1265a cathode. A signal was observed at m/z=60 that indicated contribution at m/z=100 from $^{60}Ni^{40}Ar^+$. The ^{60}Ni isotope is present at 108 ppm and the contribution at 100 AMU due to NiAr would be expected to equal ca. 300 ppb.

In a parent ion scan, Q1 scans a selected mass range that corresponds to the m/z axis of the mass spectrum. The ions sequentially enter the collision cell where those of polyatomic nature are subjected

to CID. The resulting ion beam is transmitted to Q3 which is tuned to pass only one m/z to the detector. This technique can be used in elemental mass spectrometry to identify those masses that have contributions from a polyatomic ion formed from the species selected by Q3. This mode was used to observe parent ions that would yield fragment ions of Fe. Q1 was scanned from 58 to 160 AMU and Q3 passed m/z=56. In addition to the strong indication of $FeAr^+$ (m/z=96), ion signals are observed at m/z=80 and 136 which are attributable to FeC_2^+ and $FeAr_2^+$ species respectively.

The final MS/MS technique employed in the investigation of polyatomic ions encountered in GDMS was neutral loss spectrometry. This technique permits identification of polyatomic ions containing a particular neutral fragment. This permitted identification of those polyatomic ions that arose from the combination of a metal and a species of larger ionization potential. This experiment was run to observe species that lose the equivalent of 16 m/z units. The spectrum is expected to indicate the m/z values where polyatomic ions containing ^{16}O will appear. The major signals observed were $H_2O_2^+$ at m/z=34, CO_2^+ at m/z=44, CO_2H^+ at m/z=45, O_3^+ at m/z=48, and ArO^+ at m/z=56. This technique may find the greatest application in the confirmation of polyatomic ion identification on the basis of parent and daughter spectra.

2. Study of Oxide Samples and Getter Reagents

As an elemental analysis technique, GDMS requires a measurable atomic population of the analyte. With metal oxide (M_mO_n) samples, detected ions are a mixture of both elemental (M^+) and monoxide ions (MO^+). Our study indicates that the elemental population is dependent on the chemical environment in the glow discharge, a medium affected by gaseous impurities in the ion source, e.g., water, and sputtered reactive species from the analytical cathode.

In order to eliminate the "water problem" inherent to the oxide sample preparation, getter reagents were used as the cathode host matrix and have demonstrated the ability to enhance the elemental population of the analyte. Individually mixed with La_2O_3 in the ratio of 9:1, six conducting materials (Ti, Ta, W, C, Cu and Ag) were evaluated as to obtaining the highest $La^+/(La^+ + LaO^+)$ ratio (termed R in the following test). As shown in Table I, the tested elements present an increasing R value in the same order as their reported gettering ability, Ti > Ta > W > C > Ag Cu.

Table I. Comparison of the $La^+/(La^+ + LaO^+)$ ratio obtained in different sample matrices

Matrix Material	$La^+/(La^+ + LaO^+)X100\%$
Ti	99%
Ta	90%
W	88%
C	50%
Ag, Cu	30%

The practical significance of this study is that samples mainly composed of metal oxides, e.g., geological samples, can now be analyzed with reduced monoxide interferences. This improvement

is demonstrated in Figure 2. Figure 2A is obtained from a mixture containing minor amounts of Ag, Nb_2O_5 and ZrO_2 in a Cu matrix; Figure 2B, a Ta matrix. It is shown in Figure 2A that the isotopic ratio of Ag (m/z=107, 109) is severely distorted by monoxide interferences at the same m/z numbers, $^{91}Zr^{16}O$ and $^{93}Nb^{16}O$. The Ta matrix (Figure 2B), in which the majority of the metal oxides is dissociated, presents a spectrum with correct Ag isotopic ratio.

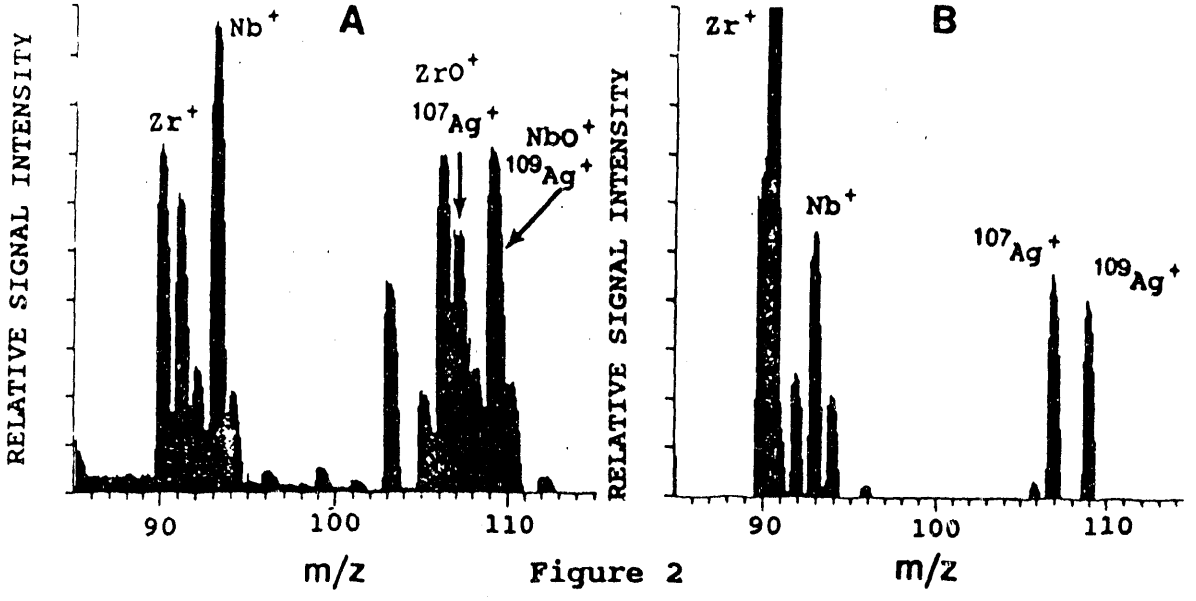

Figure 2

The incorporation of getter reagents with the analysis of metal oxides also provides a means to study some of the fundamental processes in the glow discharge. Researches were conducted to elucidate effects of gaseous impurities and getter reagents on the redox reaction between La and LaO in the plasma.

A principal component of the gaseous impurities that need to be removed is water, which contains oxygen, hence favors the oxidation of La to LaO. By competing with La for the available oxygen, getter reagents enhance the desired reduction of LaO to La. The removal of water and enhancement of La in a getter discharge, Ti, is illustrated in Figure 3. The La^+/LaO^+ ratio gradually increases as Ti removes the large quantities of water vapor, indicated by the decreasing ratio of H_3O^+/Ti^+. The large TiO^+ formed initially, changing to a much smaller, steady-state TiO^+ with time, indicates that the concentration of oxygen from the intrinsic water vapor is much larger than from the sputtered oxygen from the oxide.

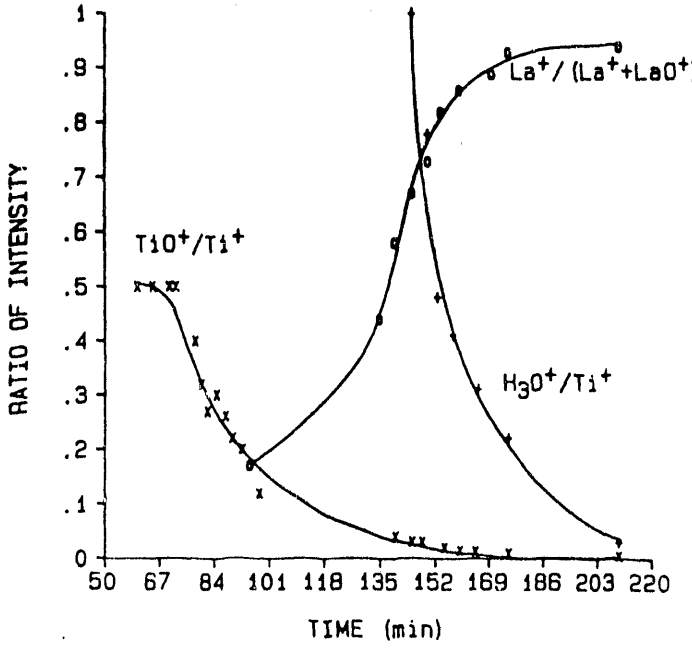

Figure 3

If Ti competes with La for the available oxygen, the concentration of Ti in the plasma should have an effect on the relationship between the R ratio and sputtering time needed to optimize the R ratio. Three mixtures were studied containing decreasing proportions of Ti getter: (a) 10%La_2O_3/90%Ti, (b) 20%La_2O_3/80%Ti and (c) 50%La_2O_3/50%Ti. Figure 4 shows the increase in sputtering time required to maximize the R ratio as the concentration of Ti in the electrode (and in the plasma) decreases.

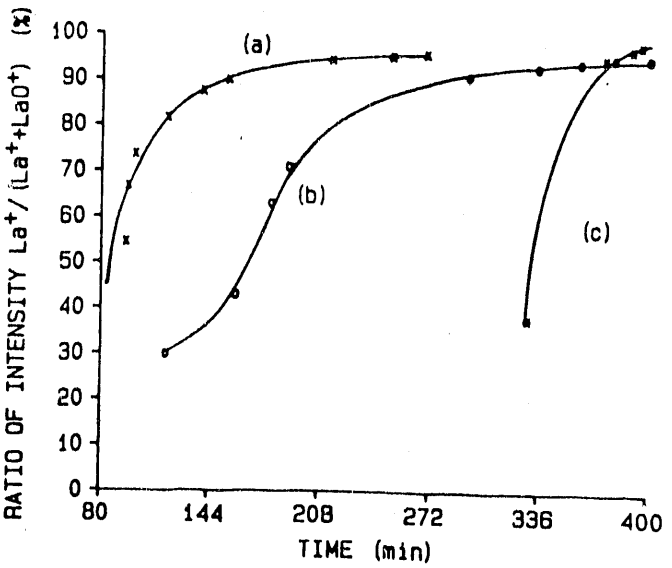

Figure 4

The selected matrix materials exhibit different degrees of efficiency in creating a large atomic La population, reflecting their respective abilities to dissociate sputtered LaO and to prevent oxygen-carriers from reacting with La. This action may be a function of a number of factors associating with the host metals, e.g., M-O bonding energy, redox reaction rate, and sputtering rate of the host matrix. Based on the previous competitive reaction theory, a matrix metal offering high sputter yield and strong bonding tendency toward oxygen is desirable for obtaining a large monatomic population of the analyte. Table II lists M-O bonding strengths and sputter yield values for the five matrices used in this study. The different gettering abilities exhibited by these metals appear to be a manifestation of factors listed here. Overall, the best getter reagents, Ti and Ta, have a good combination of both strong M-O bonds and good sputter yields.

Table II. Comparison of ionization energy, oxide bond strength, and sputter yield of sample matrices.

Elements	1st Ionization energy (eV)	M-O bonding energy (eV)	sputter yield (ions/atom)
Ti	6.82	6.92	0.42
Ta	7.89	8.36	0.45
W	7.98	6.73	0.50
C	11.26	11.18	0.10
Ag	7.58	2.33	2.70

3. Pulsed Glow Discharge Mass Spectrometry

Pulsed direct current (DC) glow discharges were originally developed in our laboratory as a method to increase applied current and sputtered yields without overheating the sample material. In addition to improving ion signal intensity, reproducible time dependant anomalies have been observed in the ion signal profiles of pulsed discharges. Preliminary work indicates that the pulsed discharge has applications as an analytical technique and as a tool to study fundamental mechanisms controlling the glow discharge.

Two distinct types of ion profiles are observed in the pulsed glow discharge. Figure 5A illustrates the shape of the applied voltage as it follows a pulsing square wave. The signal in Figure 5B is observed for contaminant gas ions (e.g., H_2O^+ and N_2H^+), and the signal for sputtered analyte ions is shown in Figure 5C. These traces were accumulated in a 1 Torr argon discharge, pulsing at 50 Hz, with a 50 % duty cycle.

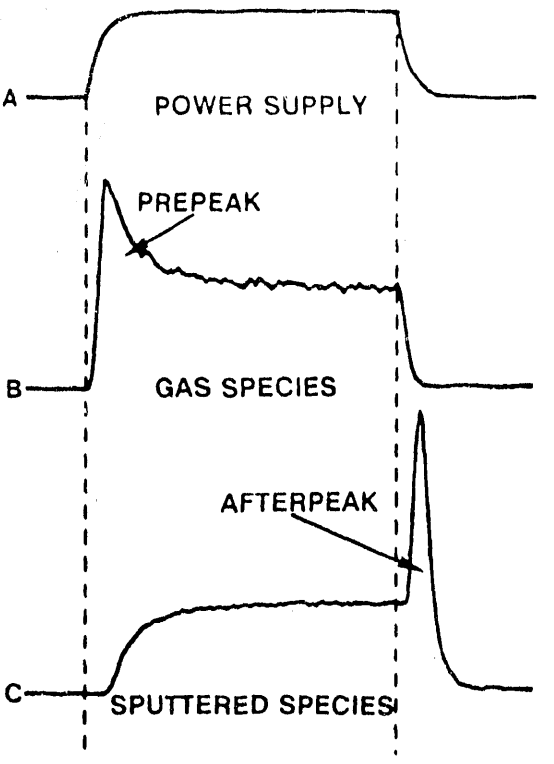

Figure 5

The distinguishing feature of contaminant gas signals is the prepeak, observed when the high voltage is first applied at the beginning of the pulse period. Contaminant gas signals begin to appear at ca. 0.3 msec after applying the high voltage and approximately 0.5 msec before the sputtered species. The position of the sample relative to the exit orifice does not alter the timing of the prepeak, indicating the effect is not associated with the diffusion of material sputtered off the sample. High energy electrons that ionize gas species are likely responsible for prepeak formation.

High energy electrons receive their energy from the electric field created at the cathode. Therefore, to study the affect of electron energy on the prepeak, it was necessary to carefully control the applied voltage. Figure 6 is a summary of the response of various ion signal profiles to a sawtooth-shaped high voltage pulse. In contrast to the abruptly changing voltage with a square wave, the slowly changing sawtooth voltage allows a correlation to be determined between electron energy, applied voltage, and the observed ion signal. In the figure, contaminant gas species, H_2O^+ (Fig. 6A) and N_2H^+ (Fig. 6B), show signal maximums between -700 and -1000 V. As the applied voltage increases at the beginning of the pulse period, the velocity of electrons accelerated by the electric field rapidly increases. The probability of an electron colliding with atoms and molecules initially increases with increasing velocity, reaches a maximum, then begins to decline. Formation of the prepeak may be tied to the changing electron collision probability as the voltage increases at the beginning of the pulse - a process easily observed with sawtooth waveforms. These data not only indicate a possible mechanism for formation of the prepeak, they also imply there is a minimum voltage at which to operate glow discharges. Since the optimum collisional cross section for electrons to ionize gas species is between -700 and -1000 V (at 1 Torr argon), operating the glow discharge at voltages in excess of -1000 V should decrease the intensity of contaminant gas signals in the mass spectrum.

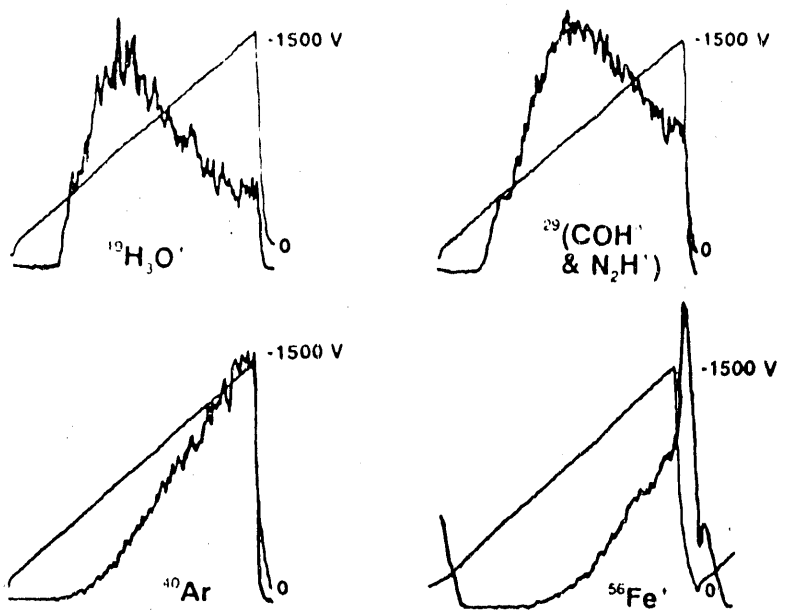

Figure 6

Following the prepeak region, signals for both sputtered species and contaminant gases reach a plateau value similar to a DC discharge. During this time in the pulse period, ion formation is a balance between electron impact and Penning ionization mechanisms. In order to maintain the same average current in a pulsed discharge as a DC discharge, the voltage must be increased to compensate for the periodic time that the discharge is off. Because of this higher voltage, the ion energy in the pulse plateau region is slightly higher than in DC discharges.

When the discharge is terminated at the end of the pulse period, the supply of energetic electrons is eliminated and the gas species signals decay to the baseline. Sputtered species signals, however, show a rapid increase in intensity (the afterpeak), reaching a maximum well above their plateau value in less than 1 msec before decaying to the baseline. The loss of energetic electrons, coupled with the selective nature of the afterpeak, points to ionization by metastable atoms of the discharge gas (Penning ionization) as the key mechanism in the post pulse region.

Afterpeaks are observed only for atoms and molecules with ionization potentials lower than the metastable energy level of discharge gas atoms. Argon has two metastable energy levels, 11.5 and 11.7 eV. Hence, Penning ionization by argon can occur for all transition elements, but not for contaminant gases such as H_2O, O_2, and COH that have ionization potentials above the metastable energy levels of argon. This explains why contaminant gases do not exhibit afterpeaks in the post pulse region.

In order to verify the role of sputtering gas metastable atoms in afterpeak formation, an alternative discharge gas with metastable energy levels different than argon was used in a pulsed discharge. Neon was selected because its metastable energy levels (16.6 and 16.7 eV) will ionize common contaminant gas species. In a pulsed neon glow discharge, both sputtered species and

contaminant gases show afterpeaks in the post pulse region.

Differences in the shape of various ion signals make it possible to discriminate against certain species by selectively collecting data at different times during the pulse period. Figure 7 illustrates how collecting data through a narrow gate during a pulse influences the observed spectrum. Figure 7A is a d.c. mass spectrum of a brass pin. Figure 7B is a spectrum from the same pin using a pulsed discharge and collecting data 1 ms after applying the high voltage; the result is a decrease in the sputtered species ion signals. Figure 7C shows the effect of collecting data for 1 ms after termination of the pulse; here sputtered species and argides are emphasized and gas signals are reduced.

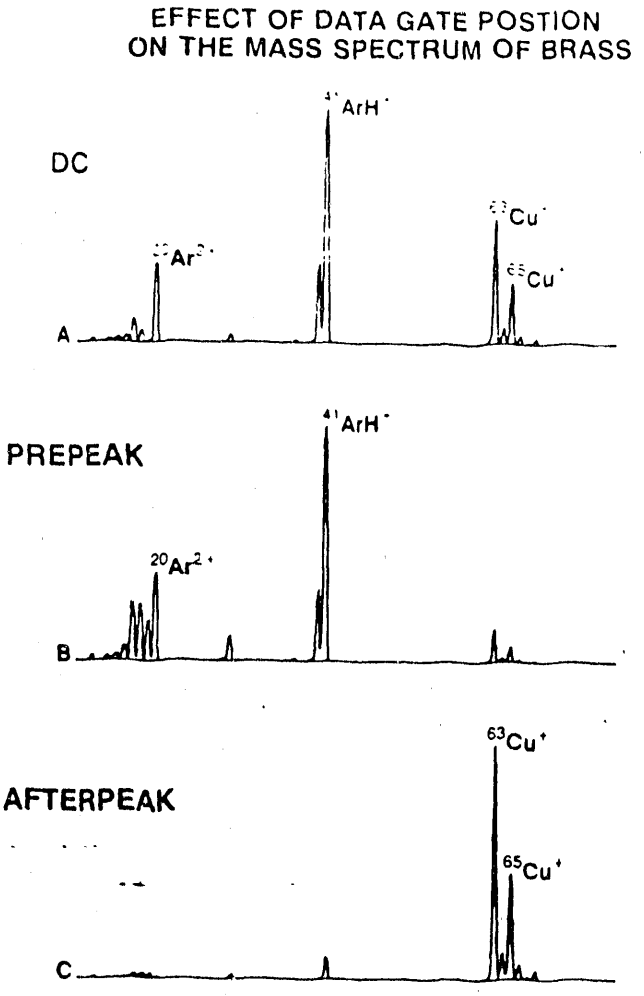

Figure 7

This technique has been successfully applied to the silicon region of the mass spectrum where troublesome gas species such as COH^+ and N_2H^+ overlap Si isotopes. By collecting data late in the afterpeak, the gas species can be reduced to show the Si isotopes to within 1% of their accepted values.

4. Electrothermal Atomization of Solution Samples

GDMS has only found limited use as a method for the analysis of solution samples. Solution analysis in the glow discharge has not been pursued to a great extent because there are other techniques that are normally more suited for solution analysis (such as ICP). On the other hand, a solution analysis technique like ICP requires extensive sample preparation (i.e., acid dissolution) if the method is applied to solids. One of the drives for this project is for the analysis of small volume solution samples to enhance the GDMS technique and expand its capabilities so that it may be recognized as a method of analysis for both solid and solution samples.

There are several methods that may be applied for the analysis of solutions in the glow discharge. The first problem is the introduction of these samples into the high vacuum environment. The presence or introduction of solvents into the discharge

chamber will affect the plasma and may even extinguish it. Even if the solvent amount is very small, its presence may alter the ionization processes in the plasma. An initial experiment in this laboratory involved the deposition of a small amount of solution onto a cupped discharge cathode. The solvent was evaporated leaving a thin layer of the solution residue containing the analytes of interest. The cathode was then placed into the vacuum chamber and the residue analyzed like any other surface species on a sample by sputter atomization into the discharge. The problem with this technique was that sputter atomization is slow and the capability for low detection limits were hampered. The research performed in the current project uses an electrothermal filament to atomize quickly the solution residue into the discharge for ionization and subsequent detection with the mass spectrometer.

Electrothermal atomization of an element on a surface occurs when the element is heated to a temperature above its vaporization (or atomization) point. This causes neutral elemental species to be removed from the surface and allows them to diffuse away from the surface. In the experiments performed in this laboratory the electrothermal element is a rhenium ribbon on which the solution is deposited and evaporated. The solution residue, containing the analytes under study, is then electrothermally removed from the filament and introduced into the discharge. The atomic population that is produced will then be ionized by the discharge and detected with the mass spectrometer.

The solution samples for these studies were prepared by mixing an appropriate amount of a metal nitrate with distilled water to obtain a cation concentration of about 1000 ppm. These preliminary studies use a high analyte concentration in an effort to develop the conditions for further analytical work at lower concentrations. The atomization source is constructed from a 0.1 mm by 0.8 mm rhenium ribbon coiled 2-3 turns around a metal rod. The final loop dimensions are ca. 2.75 mm long and 4 mm in diameter. The filament is attached to a direct insertion probe (see Figure 8) in a manner such that the center of the coil is aligned co-axially with the exit orifice of the ion source. The analysis takes place as follows: 1) pipet 15 microliters of the sample into the center of the filament; 2) evaporate the solvent with 1.4 mA of filament current for 2 minutes; 3) place probe in high vacuum (10^{-4} Torr) for 2 minutes; 4) introduce argon at the working pressure (1 Torr); 5) turn on the discharge for 5 seconds for stabilization (discharge running at 500 volts constant); 6) atomize the solution residue with 4 amps filament current; 7) collect the transient signal on a multi-channel analyzer and turn off the discharge; 8) heat the filament for 3 minutes for complete sample removal and to minimize memory effects; 9) allow the filament to cool for 5 minutes.

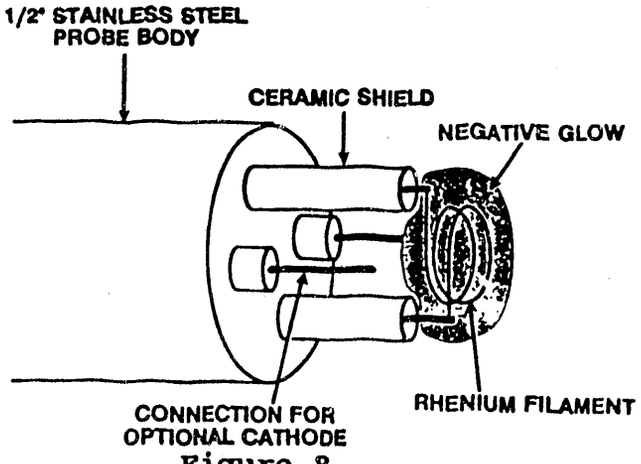

Figure 8

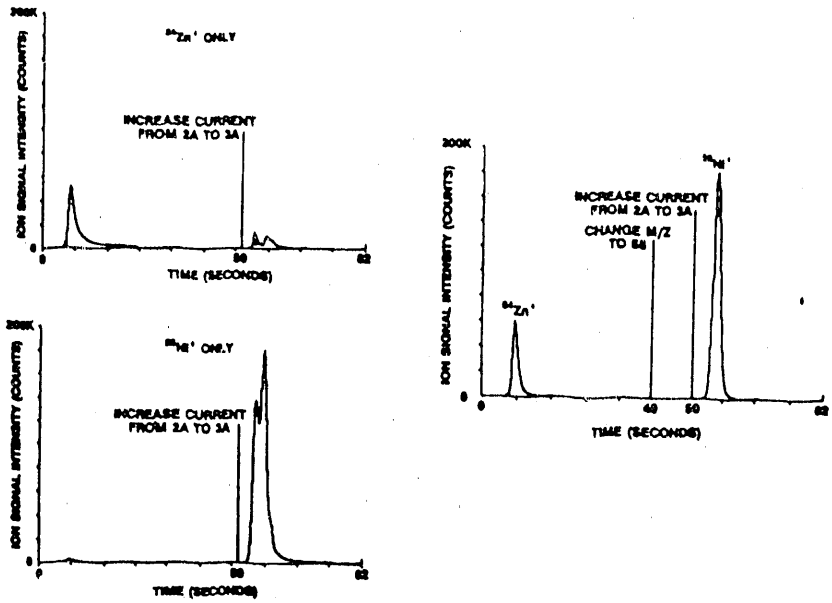

Figure 9

The results obtained thus far give good indication that this technique is applicable to solution analysis in the GD source. Single element and binary element samples have been studied thus far. For single element samples, the mass spectrometer is set to pass only one m/z to the detector and the transient signal is monitored and the data analyzed by either peak height or peak area. For a binary mixture (data shown in Figure 9), the current required to atomize each element indivi'ually must be at least a few tenths of an ampere apart. In this example, zinc and nickel are separated because Zn atomizes at 2 amps filament current while 3 amps is required for Ni. The profiles for each element alone are shown as well as that for the analysis of both elements from one solution aliquot. For this procedure the mass spectrometer is set at m/z=64 and the current to 2 amps until the Zn signal subsides then the m/z is changed to 58 and the current increased to 3 amps for Ni analysis.

One important question that merits further investigation is the effects that the current running through the filament will have on the discharge conditions and its processes. At this time it is not totally clear. Initial experiments were

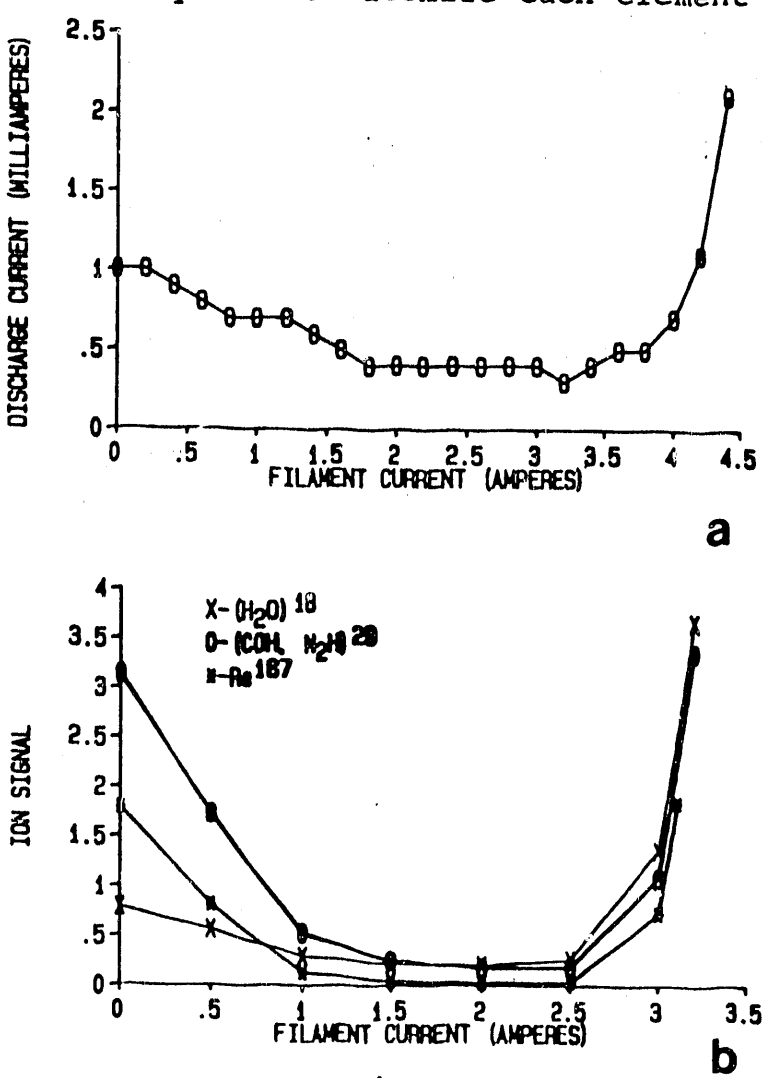

Figure 10

performed using a stainless steel pin cathode placed in various places around the atomization filament. The ion signal from the pin was decreased upon initiation of the filament current in all cases, although the greatest signal was obtained with the cathode located beside the filament. The data shown in Figure 10A (with the rhenium filament serving as the discharge cathode) shows that the filament current will suppress the discharge current up to a point, then there is a sharp increase in the discharge current. This is also reflected in Figure 10B that shows the ions signal of two gaseous species and one sputtered species. The ion signals follow a similar pattern as that of the discharge current. One possible explanation is that at the higher currents the large flow of electrons from the filament will enhance the ionization, although the effects on Penning ionization have not been studied in this system. Analyte signals from solutions will respond differently depending on their atomization temperature.

Another important piece of information that may be gathered from this technique is this laboratory's on-going interest in decoupling the atomization processes from the ionization processes in the plasma. In this particular experimental set-up, the atomization is mainly due to the electrothermal filament (with only a small amount of sputter atomization) while the ionization appears to be entirely due to the glow discharge. No ion signal has been observed from the filament without the discharge. This may provide useful information about the atomization and ionization processes in the discharge, since the source of atomization may be moved away from the glow discharge if an alternative cathode is used.

5. Radio Frequency Glow Discharges

Radio frequency (RF) glow discharges are an alternative to conventional direct current (DC) discharge as a method to atomize and ionize solid samples for mass spectrometric analysis. RF discharges are unique in their ability to sputter non-conducting materials without mixing the sample into a conducting matrix. This ability to sputter non-metals stems from differences in how electrons and ions respond to the oscillating RF voltage - a property that also makes the RF discharge more difficult to characterize than its DC counterpart.

The project reported here addresses some of the problems associated with characterizing and controlling RF glow discharges. Interactions between operating frequency, discharge pressure, and induced DC bias are some of the key factors that must be investigated to order to understand RF glow discharge.

When an electric potential is applied to a nonconducting sample, the material will act like a capacitor. As the applied RF voltage drives the sample negative, positive ions begin to bombard the surface. Before the sample potential can reach zero, however, the applied RF voltage changes polarity to a positive value and electrons begin to strike the surface. Because electrons are more mobile than ions, the surface potential quickly decays to near zero. As this process repeats itself, the difference in mobilities between the electrons and ions builds up an average negative charge

on the sample (called the DC bias). The DC bias allows the sample to be almost continuously bombarded by positive ions that sputter analyte atoms into the discharge. Conducting samples can also be sputtered with an RF discharge provided a blocking capacitor is placed between the RF power source and the sample to make the conductor act like a nonconducting sample.

Throughout the work reported here, the DC bias is used as a reference point. This is because argon ions are accelerated toward the sample surface by the electric field created by the DC bias. Hence, factors affecting the induced bias are crucial to RF discharges.

The affect of pressure on the DC bias was examined over a range of 0.3 to 1.2 Torr argon. Figure 11A shows the amount of power required to maintain a constant -1000 V DC bias as the pressure is varied. Increasing the pressure decreases the DC bias, requiring an increase in the applied voltage to maintain the -1000 V bias. This pressure relationship is the result of the flux of ions arriving at the dark space. At higher pressure, an increased number of argon ions are available to neutralize a greater percentage of the charge present on the sample surface, reducing the observed DC bias. To compensate for the enhanced charge neutralization at higher pressure, the applied power must be increased.

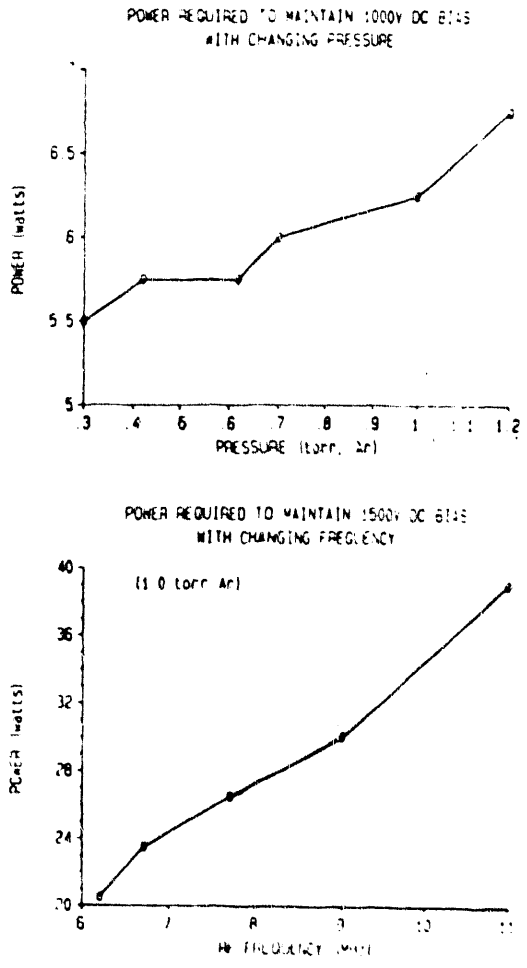

Figure 11

Another parameter that can have a significant effect on the DC bias is the operating frequency of the RF discharge. As indicated in Figure 11B, the power required to maintain a -1500 V DC bias increases as the operating frequency increases (at a constant pressure of 1 Torr argon). This response to frequency reflects the capacitative nature of the impedance present in a RF glow discharge. Because the impedance of a capacitor is frequency dependant (and decreases as frequency increases), the DC bias on the sample is easier to dissipate at higher frequencies because of the reduces capacitative impedance in the discharge and blocking capacitor. The applied power must be increased to compensate for the improved voltage dissipation characteristics at higher frequencies to maintain the desire DC bias.

Based on the above data, the DC bias is maximized when the RF glow discharge is operated in the lower MHz frequency range and lower pressures (less than 1 Torr).

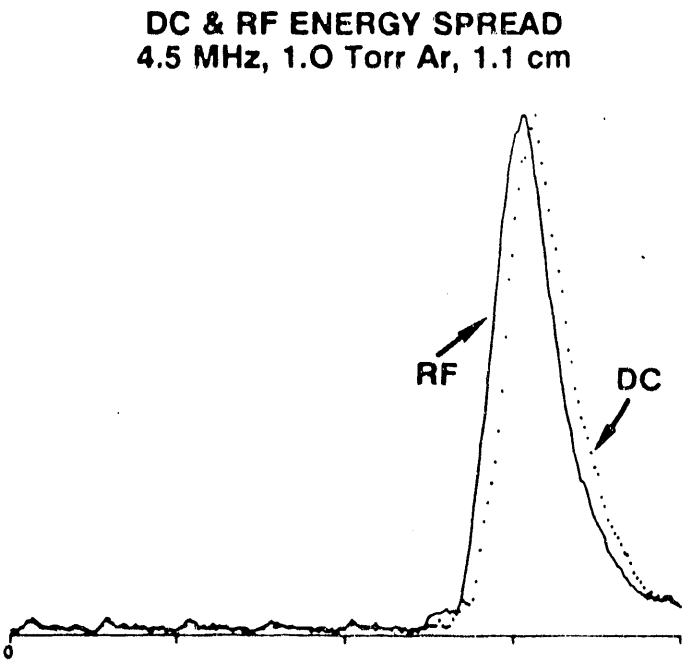

Figure 12

The usefulness of the RF discharge as a atomization and ionization source for analytical mass spectrometry was evaluated by comparing RF ion signals with mass spectra obtained with a DC discharge. (The DC discharge makes a ready reference point because it has been used longer and is better understood than RF discharges.) The first order of business in making such a comparison was to determine operating conditions where the two discharges are the most similar. This was done by examining the energy distribution of sputtered ions in both discharges; RF ions were observed to be more energetic than DC ions, a property that requires different instrument optimization settings to obtain representative mass spectra. Operating the instrument at different parameters between discharges might compromise the comparison, therefore it was necessary to find acceptable operating conditions for both DC and RF discharges. Operating the RF discharge such that the number of collisions experienced by atoms in the RF discharge reduces the average energy of the ions to a level very close to DC ions. Low MHz frequencies, higher pressure (near 1 Torr argon), and long sampling distances (ca. 1.1 cm) yield conditions where DC and RF ions have the same energy (Figure 12).

Figure 13 shows the intensity of observed ion signals relative to the applied voltage in DC and RF discharges. For contaminant

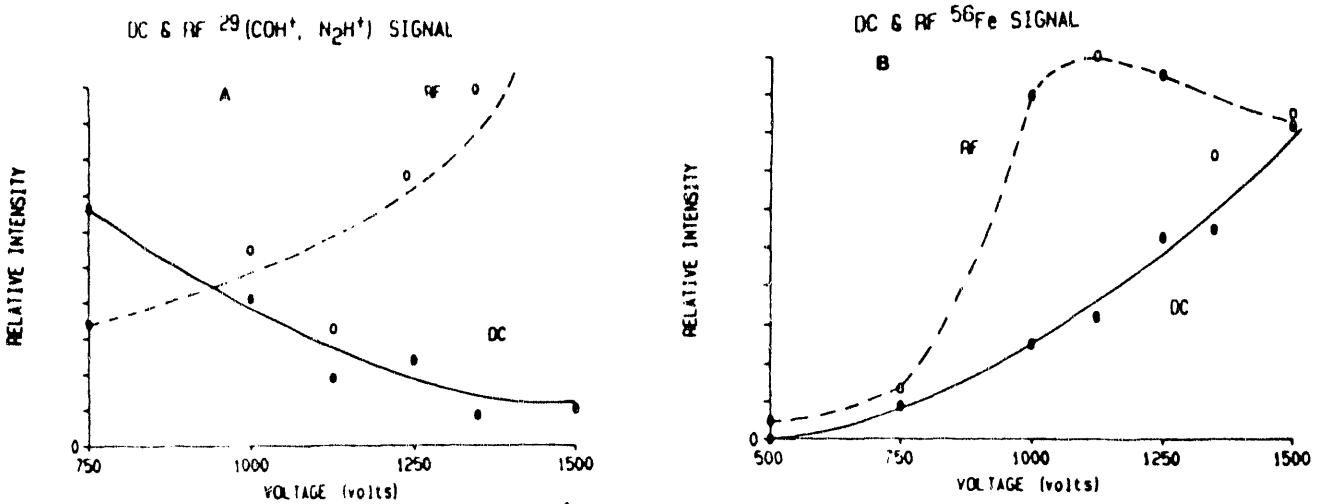

Figure 13

gas species (Fig. 13A), increasing the DC voltage yields a decrease in the observed gas signal. This is in contrast to contaminant gas signals in the RF discharge which steadily increases with the DC bias. This effect may result from increased electron impact ionization occurring in the RF discharge as the electrons respond to the increasing amplitude of the oscillating electric field.

Sputtered analyte signals also appear to be consistently higher in the RF discharge than DC (Fig. 13B). RF and DC analyte signals appear to converge above -1250 V, though it is uncertain if the RF sample is overheating at the higher power levels. Nevertheless, RF discharges do appear to yield higher ions signals than DC discharges, but with increased interfering contaminant gas ion signals as well.

END

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