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Elemental speciation using pulsed Glow Discharge Time-of-Flight Mass Spectrometry

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Elemental Speciation Using Pulsed Glow Discharge Time-of-Flight Mass Spectrometry

Na Zhang

**Dissertation submitted to the Eberly College of Arts and Sciences
At West Virginia University
In partial fulfillment of the requirements for the degree of**

**Doctor of Philosophy
In Chemistry**

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2009**

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ABSTRACT

Elemental Speciation Using Pulsed Glow Discharge Time-of-Flight Mass Spectrometry

Na Zhang

Elemental speciation analysis is very important because the toxicity of the elements is dependent on their chemical structures. The coupling of Gas Chromatography (GC) with pulsed Glow Discharge Time-of-Flight Mass Spectrometry (GDToFMS) provides real time speciation of volatile organic selenium compounds. The millisecond pulsed glow discharge is a versatile ion source for the determination of elemental composition, molecular structure, and molecular identification. The utility of this ion source to monitor a mixture of the selenium compounds dimethyl selenide (DMeSe) and dimethyl diselenide (DMeDSe) is illustrated in this work. Following the separation by GC, the compounds are readily characterized by pulsed GDToFMS. Time-gated acquisition provides unique information from three separate time regimes - elemental composition from the prepeak, structural fragments from the plateau, and intact molecular identification from the afterpeak.

Distinguishing and quantifying the specific oxidation states of elements are very hard to achieve for solid samples since specific extraction procedures tend to change the speciation. Therefore direct speciation in solid materials is highly desired.

In the present work, a pulsed glow discharge time of flight mass spectrometry method is developed for the direct speciation of chromium in solid state samples. Careful tuning of the operating parameters yields the plasma chemistry that favors cluster ion formation. Unique mass spectral features permit differentiation between the trivalent and hexavalent forms of chromium, (CrIII) and (CrVI) respectively, in chromium oxide samples. Specifically, signals at 104 and 120 m/z corresponding to the Cr_2^+ and Cr_2O^+ cluster ions are indicative of the presence of Cr(III) in the sample, whereas signal at 100 m/z corresponding to the CrO_3^+ cluster ion is indicative of the presence of Cr(VI). The impact of glow discharge operating conditions on the appearance of these characteristic cluster ions is discussed.

Also, pulsed glow discharge Time-of-Flight mass spectrometry is used to differentiate between manganese (IV) dioxide and manganese (II) monoxide in solid sample directly. Under certain conditions, the specific cluster ions Mn_2O_3^+ can be produced in the manganese (IV) dioxide glow discharge plasma. The spatial and temporal characteristics of glow discharge source are evaluated and optimized. The glow discharge operating parameters, such as the glow discharge gas pressure and the glow discharge operating power are studied and optimized. After optimizing all the related parameters, the two oxides can be differentiated easily and quantitative analysis was performed successfully.

DEDICATED TO

My parents, husband, daughter, and son

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Chapter 1

Introduction

1.1 A Historical Outlook

Since the very beginning, mankind has been curious about the nature of the world in which he lives. About 200 years ago, John Dalton proposed that all matter is composed of elements, each element consisting of a unique atom with a measurable physical property, atomic weight, and that these atoms can join together to form chemical compounds.¹ Before 1900, what elements and chemicals are present in the universe and their fundamental nature were the questions the chemists wanted to explore. Therefore, much of early chemistry is analytical chemistry, which makes analytical chemistry the mother of modern chemistry.² With the discovery of more new elements, elemental analysis was developed by Justus Von Liebig.³ Robert Bunsen and Gustav Kirchhoff were the first to suggest finding and analyzing new elements by spectral analysis. In 1860, they developed the first instrumental analysis flame emission spectrometer, by which Rb and Cs were discovered.⁴

After 1900, analytical chemistry grew quickly as a science and most of the major advances took place. Instrumental analysis gained much attention and now dominates modern analytical chemistry.⁴ Optical spectroscopic techniques, including atomic emission spectrometry, were developed in the early 20th century to characterize and

identify the elements. By measuring and interpreting radiation absorbed or emitted by atomic species, which are characteristic of an element's identity, these techniques can be used to analyze the elements.⁵ Mass spectrometry as an alternative approach to these optical techniques is used to identify elements by their characteristic mass-to-charge ratio (m/z). By this technique, even isotopes can be identified.

The invention of mass spectrometry (MS) can be tracked back to Eugen Goldstein's observation of "positive rays" (positive ion beams) in low-pressure gas discharges in 1886.⁶ Goldstein found that these positively charged anode rays, which he called "Kanalstrahlen" (English translation being "canal rays"), traveled through the channels in the opposite direction of the negatively charged cathode rays. In 1898, Wilhelm Wien found that the path of canal rays can be deflected or affected by applying magnetic fields and these canal rays were positive since their deflection was opposite to that of cathode rays.⁷

English scientist John Joseph Thomson, better known as J.J. Thomson, is called "the father of mass spectrometry" for his creation of the "Mass Spectrograph" in 1905. When he studied these canal rays, he used a low pressure glow discharge device interfaced with an electric field in a magnetic sector, that allowed ion beams to be separated according to different mass-to-charge (m/z) ratios and a mass spectrum was detected for the first time on a photo plate. In his device, isotopic composition of stable elements (^{20}Ne and ^{22}Ne) was determined.⁸

Thomson's student, Francis Aston, made significant progress in instrument design based on the first mass spectrometer. He separated electric and magnetic fields and applied a better vacuum, which led to the development of a second and third instrument with improved mass resolving power and mass accuracy.⁹ These instruments employing electromagnetic focusing allowed him to prove the existence of isotopes by mass spectroscopy and identify 212 naturally occurring isotopes.¹⁰ Aston received the Nobel Prize in chemistry for his work in mass spectrometry and isotope determination in 1922.

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In 1935, Arthur J. Dempster developed the first "scanning" MS, in which the separation of ions in a magnetic field was related directly to the m/z ratio.¹² A mass spectrum was acquired by changing the electric field of the electric sector. Later he detected the first molecular spectrum using an electron impact source and developed a spark source for the direct ion generation of metals.¹³ Based on the contributions of both Dempster and Aston, the first commercial MS was introduced to the market in 1948.

The introduction of spark source mass spectrometry (SSMS) offered a technique for the direct atomization and ionization of solid samples. This ionization method was characterized by its low detection limits and its multi-element capability.¹⁴ Unfortunately, non-continuous ion generation and instability of the source led to poor precision and accuracy. The rebirth of GD ion sources for MS was initiated by J. W. Coburn and W. W. Harrison in the 1970s due to the industry's analytical needs.^{15,16,17} They found that glow discharge can be sampled successfully by MS and the acquired mass spectrum reflected

the composition of the cathode material because the glow discharge atomized and ionized the solid cathode.

Glow discharge mass spectrometry (GDMS) has numerous advantages over SSMS. First, the GD source is much more stable than SS. Second, the atomization and ionization processes in GD are separated in space and time. Matrix effects are minimized and variations in sensitivities are minor. Therefore direct quantitative analysis of solid samples is possible by GDMS.¹⁸ Both Coburn and Harrison's pioneering work have made GDMS a leading elemental analysis method for solid samples.

1.2 Glow Discharge

1.2.1 Glow Discharge Processes and Plasma Structure

A glow discharge is initiated by a potential difference between two electrodes in a low pressure environment. In its classic and simplest structure as shown in Figure 1.1, the glow discharge device consists of two electrodes in a cell held at a reduced pressure (0.1–10 Torr). The cell is typically filled with a noble gas, for example, argon, but other gases can also be used. An electric potential of 250-2000 volts is applied between the two electrodes, which exceeds the necessary energy to break down the discharge gas. When the discharge support gas, argon in our case, is broken down positively charged Ar^+ ions and negatively charged free electrons form. Free electrons are accelerated from the

cathode to the anode, colliding with argon atoms in the discharge gas along the way. More argon ions and new electrons are produced as a result sustaining the discharge.¹⁹

The argon ions are then accelerated toward the cathode and strike the cathode surface in a process named cathodic sputtering. When the argon ions collide with the cathode, kinetic energy is transferred from the incident ions to the cathode surface. If the surface species gain enough energy to overcome the lattice binding energy they are ejected out. As a result, the process can release neutral cathodic atoms, clusters, ions, photons and secondary electrons. These secondary electrons continue to collide with argon atoms, creating new argon ions and electrons thereby sustaining the glow discharge plasma.²⁰ In analytical configurations of a glow discharge plasma, the samples to be analyzed usually serve as the cathode and the grounded glow discharge cell serves as the anode. In the glow discharge chamber, after electrons impact discharge gas atoms, excited electrons relax and emit photons giving the plasma its characteristic glow.²¹ The argon glow discharge plasma emits a blue glow as a result of excitation processes.

Figure 1.1 Classic glow discharge structure

Glow discharge plasma is a partially ionized gas, which consists of equal numbers of positive and negative charges, and a different number of neutral atoms and molecules.¹⁹ Among these species, neutral gas atoms or molecules dominate because of the low degree of ionization within the plasma. Positive ions, electrons, and photons can also be obtained. Compared with other plasma sources, such as inductively coupled plasmas (ICP), the glow discharge (GD) is compact and operates at low power. The cost to build and maintain a GD ionization source is less than ICP.²² As a “hot” plasma, ICP has neutrals and ions of high kinetic temperatures ($\sim 10,000$ K). GD is a “cold” plasma; it is characterized by modest temperatures (~ 500 K) of neutrals and ions while the electron temperatures are high ($\sim 25,000$ - $50,000$ K).²³

There are up to eight distinct regions of a normal glow discharge (GD) plasma: Aston dark space, cathode layer, cathode dark space, negative glow region, Faraday dark

space, positive column, anode dark space, and anode glow region. These regions are divided based on the luminosity. The number and size of the regions apparent in a given glow discharge plasma are relative to the size of the chamber and the pressure of the support gas. Usually, in glow discharges employed in analytical chemistry applications only the cathode dark space (CDS) and the negative glow (NG) regions are observed between the two electrodes.²⁰

The cathode dark space (CDS) is a noticeably dark region adjacent to the cathode. The cathode dark space named such owing to its low luminosity. Accross this very narrow region, the majority drop of the potential difference between the two electrodes occurs. Therefore a strong electric field forms. Ions are accelerated and bombard the cathode surface with enough energy to eject neutral cathode species and electrons. This process is called sputtering. A sheath of positive space charge forms in front of the cathode as fast moving electrons move out of this area. In this region, the probability of collisions resulting in excitation and ionization is very small.¹⁹

The negative glow region (NG), the most well-known region for its high luminosity, is the most important region in an analytical GD plasma. As shown in Figure 1, the bright blue luminous portion of the plasma bordering the CDS is the NG region. In this region, two general types of electrons exist, energetic (fast) secondary electrons and thermalized (slow) electrons. They have different functions. The energetic (fast) electrons, which have not lost their energy through collisions, are responsible for electron ionization and are essential to sustaining the GD. The thermalized (slow) electrons are secondary

electrons that have been collisionally cooled or created via the ionization process. This type of electron can give rise to excitation and recombination processes and is responsible for both the luminosity of the NG and argon metastable atoms that contribute to Penning ionization. The NG is essentially field free allowing charged particles to diffuse freely. The collision and ionization rich environment makes the negative glow region of use in analytical applications.

1.2.2 Atomization via Cathode Sputtering

Atomization of the sample is one of the most important steps that occur in and analytical glow discharge. Atomization is accomplished through the cathodic sputtering process of the glow discharge. Usually in a glow discharge device used for solids analysis, the sample serves as the cathode and the grounded glow discharge chamber wall serves as the anode. Cathodic sputtering effectively releases sample material into the glow discharge making it a useful atomization source for atomic absorption spectrometry²⁴ or atomic fluorescence spectrometry.²⁵ After the atomization of the sample cathode, the excitation and ionization of these sample atoms continue in the glow discharge providing its analytical utility in emission and mass spectrometries.²⁶ Sputtering is also the basis of depth-resolved analysis which has wide application in industry.²⁷

Sputtering results when highly energetic positive ions bombard a sample surface and eject the sample atoms from the surface. In glow discharge, positive argon ions

formed in discharge gas acquire kinetic energy while they accelerate across the cathode dark space region toward the sample cathode surface. When these high velocity argon ions impinge on the cathode surface, their kinetic energy or momentum is transferred into the cathode lattice. Atoms can be ejected from the sample surface if the transferred energy is great enough to exceed the lattice binding energy.

Several phenomena can be expected upon impact, which are illustrated in Figure 1.2. The process of cathodic sputtering produces several kinds of particles: atoms, small clusters of cathode material, ionic species, photons, and secondary electrons. Among which, neutral atoms are the majority of the gas-phase population which represents the sample atomic composition. The capability of generating a representative atomic population of the solid sample makes the sputtering process of great analytical importance. These atoms or clusters diffuse across the cathode dark space and enter the negative glow, where a variety of excitation and ionization processes happen. It is worth noting that species sputtered as secondary cations redeposit quickly onto the cathode because of the strong electric field, whereas secondary electrons propagate and sustain the glow discharge process.

Figure 1.2 Atomization and ionization in glow discharge²⁶

1.2.3 Ionization via Collisional Processes

After atomization in the cathode dark space region, sample atoms escape into the negative glow region, where collision processes abound. There are two types of collisions: elastic collisions and inelastic collisions. Elastic collisions only result in the redistribution of the kinetic energy between the colliding particles. Inelastic collisions lead to part of the kinetic energy transferred into internal energy, making excitation and ionization possible.

Various energetic species, for example fast electrons, excited and metastable atoms and ions, exist in the negative glow. Therefore, excitation and ionization occur through the transfer of energy via inelastic collisions with these various energetic species. The collisional processes impart a specific amount of energy into the analyte atom or molecule. If the energy is greater than the ionization potential, ionization of the analyte atom or molecule results. In addition to ionization and excitation, fragmentation and dissociation of molecules can also occur.

There are three important types of inelastic collision processes corresponding to excitation and ionization in the glow discharge: electron impact, Penning ionization, and charge transfer. Of which, electron impact and Penning ionization are responsible for more than 90% of all ionized species within the glow discharge.²⁸ Following ionization, these ions will be introduced into the mass spectrometer for analysis.

Electron Ionization

In a glow discharge, free electrons are energized almost simultaneously with the application of electric power. For their light mass and high mobility, these electrons possess high kinetic energy and are called fast electrons.²⁹ Electron ionization (EI) happens when a highly energetic electron collides with a gas phase species, atom or molecule, in an inelastic collision mode. The gas phase species is ionized and two electrons are produced, among which one electron is released upon collision and the other electron is the primary electron that has been slowed following the collision. The mechanism is shown below. The resultant electrons give rise to further ionization to sustain the GD plasma. Compared to conventional EI, which accelerates electron beams to 70 eV, EI in glow discharge is more powerful and efficient because the high applied potential, -2000 V, creates an electron beam of much higher average energy.

Charge Transfer

Certain species in a glow discharge can be ionized to M^+ via a charge transfer process by the discharge gas ions. When an argon ion, Ar^+ , collides with an atom, for example a sputtered atom, M , an electron (e^-) is transferred from the atom, M , to the argon ion, Ar^+ . Charge transfer ionization only occurs when the energy difference between the argon ion and the resulting analyte ion is small (0.2 eV).

Therefore charge transfer is a highly selective ionization process since it requires that the potential energy of M^+ closely matches the ionization potential of argon (15.67 eV).²⁰

Penning Ionization

Penning ionization is the dominant ionization process within glow discharge plasmas and accounts for 40-80% of the total ionization in a continuous analytical glow discharge.³⁰ Argon metastable atoms, used for Penning ionization, are formed by the recombination of argon ions with thermal electrons. Metastable atoms cannot relax directly to ground state by emission of a photon because the required transition is forbidden. The only way to release its inner energy is through a collision with another gas-phase species and the transfer of energy. If the energy carried by the metastable atom is larger than the ionization potential of the colliding species, Penning ionization can result. For example, in an argon glow discharge, when an argon metastable atom, Ar^m , collides with a sputtered atom, M , the atom is Penning ionized to M^+ and produces an argon atom, Ar , with an electron, e^- .

The metastable energies of argon are 11.55 and 11.72 eV. For the species being Penning ionized within an argon glow discharge, their ionization potential must be less than these values. Fortunately, these energies are great enough to ionize most of the

elements in the periodic table. Many atmospheric impurities from the discharge environment cannot be Penning ionized because of their high ionization potentials, for example, the common discharge gas argon has an ionization potential of 15.67 eV.¹⁹

1.3 Pulsed Glow Discharge as a Versatile Ion Source

The analytical glow discharge has two operation modes: continuous glow discharge and pulsed glow discharge.³¹ Continuous glow discharge relies on the application of a constant potential to the cathode. After continuous sputtering by ions and high energetic neutrals, the cathode material can accumulate power and become overheated. This can lead to cracks in the sample, thermal fractionation of analytes, and plasma instabilities.³² By applying potentials in modulated cycles consisting of a short pulse followed by a relatively longer ‘off’ period, the cathode is allowed to cool down and avoid overheating. This technique is called pulsed glow discharge. Pulsed glow discharges are generated by a pulsed (power modulated) power supply. Pulse parameters include pulse power, duration, and repetition frequency. Typical pulse parameters are hundreds of Watts pulse power, millisecond duration and less than 100 Hz pulse repetition frequencies.²⁰ Current work in this lab employs a 25 % duty cycle consisting of 5 ms of power on time followed by 15 ms of power off time. Operating power ranges from 40 to 120 Watts.

As an ion source, pulsed glow discharges produce many advantages when compared to continuous glow discharges.^{33, 34} Atomization and ionization can be

increased while reducing the sample thermal effects by pulsing the glow discharge. Ionization mechanisms and analytical species are separated temporally by time gated detection.³⁵ Therefore, signal from background impurities can be decreased. Pulsed glow discharge is a perfect fit with time-of-flight mass spectrometry because of the pulsed sampling mode of the time-of-flight. Time resolved mass spectra can be observed by pulsing the GD in combination with time-gated mass spectrometric detection. Pulsed glow discharge is also a tunable ion source; it can be tuned temporally to produce the desired chemical information ranging from the elemental to molecular level for elemental speciation.³⁴

1.3.1 Enhancement of Sputter Atomization and Ionization

Glow discharge is considered a low-power ion source, because it is usually operated at a power level of several watts. At this condition, the sputter rate and hence ionization rate are correspondingly low. Thus the analytical performance of glow discharge is affected.³⁶ To increase the atomization and ionization, a higher voltage and current can be applied. As a result, the sample cathode may soon overheat and sometimes even melt. To avoid these negative thermal effects, the average power must be controlled.³⁷ The general rule when considering the instrument development is that there is a counter balance between the capabilities of the existing instrument and the demands for analytical information. When analytical challenges outpace the capability of an existing instrument, new methodologies must be developed. It is not always necessary to invent a new instrument while facing new challenges, sometimes simple retooling may

produce improved capabilities.³³ Therefore, pulsed glow discharge is introduced as a more efficient ion source in MS.³⁸ In pulsed glow discharge, the instantaneous power can be raised up to several hundred watts, while the duty cycle can be modulated to make an acceptable average power. During the short pulse on period, both discharge current and voltage are much higher than the continuous operation. The higher voltage can make argon ions Ar^+ bombard the cathode surface more energetically. Therefore the sputtering rate is increased, about two orders of magnitude higher than the continuous mode.³⁹ Meanwhile, the higher discharge currents enhance the ionization of the sputtered atoms by increasing the plasma particle collisions. Therefore both higher atomization and ionization can be achieved, leading to more intense analytical signals. Sensitivity is improved and the detection limit is lowered by using the pulsed glow discharge technique. For example, it is reported that the signal intensity can be increased about 100-fold with the same average power input.⁴⁰

1.3.2 Temporal Separation of Ionization Mechanisms

As described previously, there are mainly three types of ionization mechanisms: electron ionization, charge transfer, and Penning ionization in glow discharge plasmas. These three ionization mechanisms happen concurrently in continuous mode glow discharges. The great advantage of pulsed glow discharge is the temporal separation of these ionization mechanisms, because different ionization mechanisms dominate different time regimes in pulsed glow discharge.³⁰ The individual ion signals have time-dependent responses enabling time resolved mass spectral differences. During different time

regimes, mass spectra represent different species. Analytical signal can be discriminated from the background interference signal by these temporal characteristics.⁴¹

During breakdown of the discharge gas or upon power onset, electron ionization is the dominant ionization mechanism. Once the high instantaneous voltage, about several thousand volts, is applied to the electrodes, the electrons gain high kinetic energy almost simultaneously and start electron ionization by inelastic collisions. The gas species existing in the plasma, such as the discharge gas argon and contaminant gases H₂O, CO₂, and N₂, are electron ionized quickly. Correspondingly, the signal intensity of these gas-phase ions exhibits a surge and reaches a maximum at this time. Therefore this time regime is called the prepeak regime,⁴² as shown in Figure 1.3. Usually in a prepeak mass spectrum, no signal attributed to the cathode material is observed. In such a short time (0-0.4 ms), the sputtered atoms haven't yet diffused into the negative glow region.

A stable glow discharge plasma forms at about 1 ms into the pulse. From this time until termination of the power, this period is called the plateau regime. The plasma at this time reaches a steady state and is equivalent to its continuous power counterpart. After the discharge gas breakdown period ends, the average electron energy decreases to about 2-4 eV. Under this condition, only a small fraction of the electron population is actually capable of ionization. Therefore, electron ionization efficiency declines in this time region. Charge transfer relies on the population of argon ions. Argon ions result from the breakdown of the discharge gas and reach a plateau around 1 ms. Thus, charge transfer ionization can happen in the plateau regime too. According to a study by King's group,⁴³

argon metastable atoms appear after discharge breakdown and gradually reach a steady value at about 1 ms into the pulse. This gives a clue that Penning ionization happens in the plateau regime. Therefore, in the plateau time regime (1-5 ms for a 5 ms pulse), all three ionization mechanisms happen together, which can explain the equivalence to the continuous glow discharge plasma. Both discharge gas and sputtered species appear in the plateau mass spectra.

Once the power terminates, the energetic electrons in the plasma quickly become thermalized through collisions and diffuse away.⁴⁴ No energetic electrons are produced once the electric field disappears. Thus, electron ionization halts immediately after the termination of power. The population of argon metastable atoms greatly increases in this post-pulse period because of the recombination of argon ions with thermalized electrons. Penning ionization is greatly enhanced through the existence of a large population of argon metastable atoms. Meanwhile, charge transfer extinguishes because of the deficiency of argon ions. Therefore in the afterpeak regime (5.1-6 ms for a 5 ms pulse), Penning ionization is the dominant ionization mechanism. As described previously, although argon metastable atoms are less energetic than other active species in the glow discharge, most of the sputtered species can be Penning ionized. Discharge gas species cannot be Penning ionized because of their high ionization potentials. Therefore, in afterpeak spectra, the analyte signal is enhanced while the plasma background signal is decreased or disappears all together.⁴²

Figure 1.3 Temporal characteristics of pulsed glow discharge

1.3.3 A Tunable Ion Source

In pulsed glow discharge, the internal energy deposited into the analyte molecules can be controlled. For molecular species, the molecular internal energy distribution can determine the final product ions observed. By tuning the molecular internal energy, the degree of fragmentation can be controlled to provide molecular, fragment or elemental information. In pulsed glow discharge, there are several parameters that can affect the internal energy disposition.

Temporal control of plasma chemistry can offer rapid energy tunability. As demonstrated before, the ionization mechanisms can be separated according to the different time regimes of the pulse cycle. This provides a different ionization environment for the analyte, from “hard” ionization to “soft” ionization. During the prepeak regime, analyte molecules are electron ionized to small fragments and atomic constituents by the highly energetic electron beams. Elemental information is readily available from the prepeak spectra. A look at spectra from the plateau regime reveals extensive structural information because all of the three ionization mechanisms mix together. During the afterpeak regime, ionization can be considered as “soft” and molecular information can be obtained.⁴⁵

The internal energy distribution can be tuned spatially too. The population of each energetic species and the corresponding ionization vary in different locations of the

plasma. Therefore in a certain position, the specific energy transfer processes combine together to provide a spectrum of unique information.

Other than the temporal and spatial variation, the discharge operating parameters, for example, discharge gas pressure and composition, can be used to tune the internal energy distribution to achieve the desired chemical information.

1.4 Pulsed Glow Discharge Time-of-Flight Mass Spectrometer

The pulsed glow discharge is endowed with many advantages as an analytical ion source. It is important to choose a suitable mass analyzer to fully exploit the pulsed glow discharge's advantages. Basically, a mass analyzer designed to work with a pulsed ion source would perfectly match. Time-of-flight mass spectrometry is an excellent fit because it works best with a pulsed ionization source. One of the pulsed glow discharge's characteristics is that a gated detector is required to extract the signal as a function of time. The majority of glow discharge mass spectrometers employ quadrupole mass filters or double-focusing mass analyzers. These systems are not well suited to time-gated acquisition of signals. Time-of-flight uniquely enables fast simultaneous spectral acquisition by allowing the acquisition of an entire mass spectrum with every extraction pulse.⁴⁶ Among various mass spectrometers, TOFMS has the fastest analytical speed and the highest mass transmission. TOF can be operated at a high repetition rate while a large number of mass spectra can be quickly acquired and averaged, which leads to significant S/N enhancement.⁴⁷ Based on these factors, time-of-flight mass spectrometry is

successfully coupled to pulsed glow discharge and brings many advantages to its application.

As shown in Figure 1.4, ions produced from the pulsed glow discharge are sampled by the exit orifice and extracted by the skimmer. After passing through a slit, these ions enter the extraction region defined by a repeller plate (R) and an extraction grid (G_0). The repeller, with its pulsed voltage, injects the ions at a specific time.⁴⁸ As presented in the figure, Trace A is the initial applied glow discharge power pulse, of which the frequency, duty cycle, and power level is controllable. The initial trigger (Trace B) output is positioned at the edge of glow discharge power onset. Trace C represents an internal trigger set at a certain delay time relative to the initial trigger. This delay triggers the application of a positive pulse (Trace D) with an adjustable width to the repeller. Therefore ions can be injected into the acceleration region between G_0 and G_1 , where a constant acceleration is exerted onto the ions before they enter the orthogonally positioned flight tube. By changing the temporal position of the repeller pulse, the mass spectrometer is capable of monitoring ions formed during distinct time regions in the GD plasma power pulse cycle.⁴⁶

In the flight tube ions are separated based on their differences in velocity. Since the flight tube is a field-free drift region, ions fly at a constant velocity. The different velocities of different ions can be related to differences in the mass-to-charge ratio of the particles. A detector is positioned at the end of the flight tube to record the flight times of

the ions and produce a complete mass spectrum. Mass-to-charge (m/z) ratios can be determined by measuring the time (t) that ions fly through the flight tube.

Figure 1.4 Diagram of GD-TOFMS and pulse application interpretation

In theory, the potential energy (E_p) of a charged particle in an electric field is related to the charge of the particle (q) and to the strength of the electric field (U):

$$E_p = qU$$

Where (q) is the total charge of the particle, $q=ze$, and U is the electric potential difference.

$$E_p = zeU$$

When the charged particle is accelerated into the time-of-flight tube by the voltage U , its potential energy is converted to kinetic energy. The kinetic energy of a particle with mass (m) and velocity (v) is calculated by:

$$E_k = \frac{1}{2} mv^2$$

Since the potential energy of the particle is converted to kinetic energy, meaning that E_p are equal to E_k , thus,

$$zeU = \frac{1}{2} mv^2$$

The velocity of the charged particle will not change while it moves in a field-free time-of-flight tube. Since the flight length (d) of the ion is known as the length of the flight tube, and the flight time of the ion (t) can be measured, the velocity (v) of the ion can be determined in a time-of-flight tube.

$$v = d/t$$

The value of v is substituted as follows,

$$zeU = \frac{1}{2} m(d/t)^2$$

After rearrangement, the flight time is expressed as:

$$t = d (m/z)^{1/2} / (2Ue)^{1/2}$$

These factors for the time of flight have been grouped purposely. Since $d/(2Ue)^{1/2}$ is a constant, the final equation reveals clearly that the time of flight of the ion varies with the square root of its mass-to-charge ratio m/z .⁴⁹

1.5 Chemical Speciation

The rapid increase in the levels of environmental pollution over recent decades has resulted in increasing concern for people's health and global ecosystems. In the beginning, most analytical measurements only focused on the total content of a specific element in a sample, such as toxic elements arsenic and mercury or essential elements selenium and magnesium.⁵⁰ Recently, it has been found that the toxicity of the element is highly dependent on its chemical form or chemical environment. In natural systems, the specific forms of an element determine its physical and chemical behavior. Changes in environmental conditions, such as pH, redox potential, and complex ligands, etc., can dramatically affect the behavior of both the essential and toxic elements by altering the forms in which they exist. For example, the inorganic form of arsenic is extremely toxic while arsenobetaine as a common form in fish is relatively innocuous. Also, the hydrated Cu^{2+} ion is more toxic than other copper species.²³

For these reasons, chemical speciation was quickly developed as a discipline in analytical chemistry. The term “chemical speciation” refers to the determination of the specific form of an element in a sample (eg, As, Cr, Hg, Mn species) using a wide range of analytical techniques. This area involves an assessment of health hazards, toxicity and

bioavailability based on levels of specific chemical forms, rather than on total element levels.⁵¹ Speciation science represents a broad field of study and attracts scientists from differing backgrounds such as chemistry, biology, environmental science, and geology.

1.5.1 True Meaning of Chemical Speciation

The International Union for Pure and Applied Chemistry (IUPAC) has published guidelines or recommendations for the definition of speciation analysis in 2000,⁵² which recommends the terms as follows:

“Speciation analysis is the analytical activity of identifying and/or measuring the quantities of one or more individual chemical species in a sample.”

“The chemical species are specific forms of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure.”

“The speciation of an element is the distribution of an element amongst defined chemical species in a system.”

The narrow definition of chemical species was referred to as “classic speciation” because it is perfectly appropriate to speciation of solutions, however, when it came to solid-state material such as soils, sediments, and geochemical materials, selective solid sample extraction and fractionation procedures are required. Therefore a broader

definition which encompasses the IUPAC type was developed. In this context, the term speciation was further defined as: ⁵¹

“The process of identifying and quantifying the different, defined species forms or phase present in a material.”

“The species, forms or phase are defined (a) functionally, (b) operationally, or (c) as specific chemical compounds or oxidation state.”

Functionally defined species are exemplified by the plant availability. Operationally defined species are fractions isolated by physical or chemical fractionation procedures. The third type of speciation is the hardest to achieve because it requires analytical methodology of great selectivity and sensitivity to measure the precise chemical form of an element. For solid samples, this form of speciation is almost impossible while the first two types are readily available. Although direct non-destructive methods can be employed to identify the species, it is generally unable to quantify it without separation techniques.⁵¹

1.5.2 Application of Pulsed Glow Discharge Coupled with Time-of-Flight Mass Spectrometry for Elemental Speciation

The study of elemental speciation requires multi-dimensional knowledge. Following the separation of the constituent components, the identification of each component is demanded. Therefore, extensive chemical information about the compound at the elemental, structural, and molecular level is desired. This urgent need drives the development of technology for chemical speciation.⁴⁵

Various hyphenated techniques have been developed for chemical speciation. Among which, chromatographic separation coupled with elemental or molecular determination is the most frequently used approach. Mass spectrometry is considered to be the most sensitive and selective technique to identify different chemical species.⁵³ Various levels of information can be achieved by mass spectrometry using different ionization techniques. As it is well known, ICP MS provides accurate elemental composition by its hard ionization method. Electron impact (EI) is the most common ionization method, which expresses structural information and aids identification of the compound by comparison with a library of standard spectra. Chemical ionization (CI) yields molecular information and molecular weight that can be interpreted from the mass spectrum.⁵⁴

Uniquely, each MS technique provides information of one dimension, yet all of these levels of information are highly desired. Thus, these methods have to be employed

and combined together to achieve a complete understanding of the compound. These results come at the expense of analysis duration, cost, sample size, operator skills and so on. Pulsed glow discharge as a tunable plasma ion source coupled with time-of-flight mass spectrometry is a breakthrough in the search for a comprehensive technique.⁵⁵ TOFMS is well known for its theoretically unlimited mass range, which is critical to elemental speciation, for producing molecular mass spectra in the higher m/z region. As described previously, pulsed glow discharge time-of-flight MS can provide simultaneously the elemental, structural and molecular information of chromatographic effluents.⁵⁶

In the development of improved methods for chemical speciation, it is found that the analysis of aqueous samples is heavily focused upon when, in fact, the direct elemental speciation analysis of solid samples is greatly needed. For example, within material sciences there is a demand for the in-situ characterization of the designed material. Of environmental and geochemical concern is the degree of heterogeneity encountered in a natural sample. Indeed, labile species cannot easily be separated from all solid matrices. Even when these species can be extracted, their chemical environment will be changed to some extent. Therefore direct non-destructive methods are highly desired. Pulsed glow discharge coupled with time-of-flight mass spectrometry can be employed in this important area and resolve many problems.⁵¹

This work focuses on analytical applications and theoretical studies of pulsed glow discharge time-of-flight mass spectrometry for chemical speciation. Chapter 2 is the

research of gas chromatography coupled with pulsed glow discharge time-of-flight mass spectrometry as a speciation technique for organic selenium compounds. Preliminary studies demonstrated that all three levels of information can be achieved. This is a very promising method with advanced revision. In chapters 3 and 4, direct speciation analysis in solid samples is studied. It is found that the desired plasma chemistry environment can be obtained by tuning the glow discharge plasma parameters in favor of producing the cluster ions. Specific cluster ions can be used to differentiate between different oxidation states. Manganese and chromium are studied directly in solid samples thus avoiding any tedious dissolving and extraction steps. Quantitative analysis is also performed with satisfactory results obtained. Chapter 2, 3 and 4 are individual paper manuscripts, in which the modified edition of chapter 3 has been published in Journal of Analytical Atomic Spectrometry (JAAS).⁵⁷

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Chapter 2

Real-time Chemical Speciation of Volatile Organic Selenium Compounds Using Gas Chromatography Coupled with Pulsed Glow Discharge Time-of-flight Mass Spectrometry

Abstract

Speciation analysis of organic selenium compounds is very important because the toxicity of the compounds is dependent on their chemical structures. The coupling of Gas Chromatography (GC) with pulsed Glow Discharge Time-of-Flight Mass Spectrometry (GDTOFMS) is examined for its potential to provide real time speciation of organic selenium compounds. The millisecond pulsed glow discharge is a versatile ion source for the determination of elemental composition, molecular structure, and molecular identification. The utility of this ion source to monitor a mixture of the selenium compounds dimethyl selenide (DMeSe) and dimethyl diselenide (DMeDSe) is examined in this work. Following the separation by GC, the compounds are subject to characterization by pulsed GDTOFMS. Time-gated acquisition provides unique information from three separate time regimes - elemental composition from the prepeak, structural fragments from the plateau, and intact molecular identification from the afterpeak.

2.1 Introduction

Selenium is an important element found in nature. It is essential for plant, animal and human growth. Selenium can protect cells against oxidative damage because it is a necessary component to form the active center of glutathione peroxidase and other selenoenzymes.¹ Many selenium compounds are found to exhibit chemopreventive effects with regard to cancer. Selenium compounds can ameliorate the toxic effects of heavy metals such as arsenic and mercury by catalyzing the intermediate metabolism reaction for these metals.¹ For humans, 55-70 μg daily intake of selenium is necessary. Selenium deficiency in the diet can cause diseases such as arthritis, multiple sclerosis, etc.² On the other hand, higher concentrations ($> 130 \mu\text{g/L}$) of selenium will have an adverse effect to people's health.³ It can produce chronic toxicity symptoms and cause liver carcinoma, cirrhosis, teeth, hair and nail loss, irritation of eyes and even paralysis.⁴ The range between the necessary daily intake and the toxic value is very narrow; therefore the determination of trace selenium in environmental and biological tissues has been widely studied.⁵

Compared to developments in the quantitative analysis of selenium, qualitative analysis, especially real-time chemical speciation has lagged behind.⁶ Chemical speciation is important because the toxicity, bioavailability and essential nature of selenium strongly depends on the chemical form of the compound.¹ It is necessary to study the speciation of selenium in environmental and biological samples to understand the biogeochemical cycle, mobility, transfer, uptake and toxicity of selenium.⁵

In the environment, selenium is present in different oxidation states as a variety of inorganic and organic compounds. Inorganic selenium species exist in natural water and soils as elemental selenium (0), selenide (-II), selenite (+IV) and selenate (+VI), among which selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) are most frequently found. Organic forms of selenium include volatile and nonvolatile compounds which can be found in air, organisms or in the aqueous environment. Volatile organic selenium species are methylated compounds, while nonvolatile organic species include trimethylselenonium ions, selenoamino acids, selenoproteins, and their derivatives.⁵ These organic selenium species exist in biological systems with direct covalent carbon-selenium (C-Se) bonds, not bound by coordination in contrast to metal-protein complexes.⁷ Organic selenium compounds can bioaccumulate in the body of a human or animal. It is found that inorganic species are five hundred times more toxic than organic species of selenium.⁸ Inorganic selenium can be transformed to less toxic volatile organic selenium compounds by fungi, plants and animals through microbial action. The primary pathway for the metabolism of selenium is to reduce selenium at the intrinsic ionic potential and then methylate it to methylselenol, dimethylselenide, and the trimethylselenonium ion.⁷ These biomethylation processes constitute the major mechanism for selenium detoxification, which are a form of self-protection that occurs in the biological system.³

A substantial amount of work has been done in the determination of total selenium, selenite and selenate compounds; while little work has been reported about the speciation of organoselenium compounds.¹ The study of chemical speciation of organoselenium compounds is useful to understand the metabolism of selenium in a biological system and

the toxicity of those compounds. Furthermore, the function of those compounds in the biochemical cycle can be learned. It is well documented that volatile organic species of selenium are produced by a variety of microorganisms, plants and animals as a result of selenium detoxification.¹¹ Among those volatile organic selenium compounds, dimethyl selenide (DMeSe) and dimethyl diselenide (DMeDSe) are the major metabolites of the biosystem. They are both toxic by inhalation and if swallowed under high concentration. And they both have the potential danger of cumulative effects.⁹ According to its material safety data sheet, dimethyl diselenide is more toxic than dimethyl selenide.

Generally, the speciation of volatile forms of selenium is performed by a separation technique coupled with a certain detector. Usually gas chromatography is chosen as the classic separation technique for volatile organoselenium compounds. Solid-phase microextraction (SPME) is often used for extraction, sample preconcentration, and introduction of the volatile sample onto the GC column.¹⁰ C.Dietz et.al used SPME combined with an in-house developed adsorption unit for speciation of two volatile organoselenium compounds (dimethylselenide and dimethyldiselenide) without an additional commercial chromatographic system.⁸

The choice of detector for gas chromatography depends on the desired information level. The most frequently used gas chromatographic detectors for organoselenium include flame ionization detector (FID), electron capture detector (ECD), atomic absorption spectroscopy (AAS), atomic emission detector (AED) and mass spectrometry (MS). FID is the most straightforward detector which can give the

concentration of each compound; however, it cannot provide any direct chemical information without comparing it to the retention times of standards. ECD can provide a higher level of information because it can give chemical information of some specific elements which have high electronegativities, such as S, N, O, and halogens. Thus ECD is considered to be a class-specific detector. AED can provide element specific detection. In this case, the elemental composition and empirical formula of an eluting compound can be obtained. MS can provide the greatest amount of chemical information.⁶ In C.Dietz et.al's work, the results using AAS and ICP-MS as detectors are compared. Their results showed that ICP-MS is much better than AAS in terms of sensitivity. J.L Gomez-Ariza et.al studied the speciation of volatile forms of selenium and inorganic selenium in sediments by GC-MS. They used electron impact mass spectrometry. The dialkyldiselenides samples were derivatized with 1-fluoro-2, 4-dinitrobenzene after extraction into ethyl acetate and evaporated to dryness under a N₂ stream to increase the sensitivity of DMeDSe.¹¹ Juris Meija et.al used commercial GC/MS and GC/ICPMS to analyze volatile selenium from Se accumulating plants. They used head-space SPME as the sample introduction method. They also added optional gases (O₂ and N₂) to the argon discharge to increase the sensitivity for Se.¹² Y. K. Chau et.al used GC-Atomic absorption to analyze dimethyl selenide and dimethyl diselenide¹³. Stefan M. Gallus and Klaus. G. Heuman used a GC-ICP-IDMS system to study and determine volatile selenium speciation.¹⁴

Although these methods are well developed, they cannot provide complete information of each compound in the sample at the same time. Thus real time chemical

speciation is hard to realize using current methods for Se analysis. This work focuses on the development of new methodology for selenium speciation and illustrates its potential applicability.

There are many kinds of ionization sources for mass spectrometry. And each of them has some special advantage in chemical speciation, for example, inductively coupled plasmas are good at determining elemental composition, EI is good for examining molecular structure, and CI does well in permitting identification of the molecular ion. Recently, tunable plasmas as an ionization source have been the focus of much attention because these plasmas can produce both EI and CI-like mass spectra by tuning of the operating parameters.¹⁵ The glow discharge ionization source is well established but has found new applications in the area of chemical speciation.¹⁹ It is a tunable ionization source and transfers energy to analytes via a variety of collisional processes: electron impact ionization, charge exchange ionization, and Penning ionization. Pulsed glow discharges typically operate with a series of square wave power pulses. The width of the pulse can be on the order of a few microseconds to milliseconds.¹⁶ The transient power mode can be radiofrequency (RF) or direct current (DC). Compared to DC, RF can deal with electrically insulating as well as electrically conducting samples. With pulsed glow discharges, information relating to elemental composition, molecular structure and identification of the molecule can be obtained using time-gated mass spectrometry.

The glow discharge has temporal characteristics consisting of three time regimes: prepeak, plateau and afterpeak.¹⁷ Time-gated acquisition can provide unique information from each of these time regimes: elemental composition from the prepeak, structural fragments from the plateau, and molecular ions from the afterpeak.¹² For prepeak spectra, the time gate can be set to 0-0.6 ms after plasma initiation. Because the onset of the pulse is rapid, the energy is enough to dissociate species to atoms and ionize them. For a 5 ms pulse, the plateau is considered to be between 0.6 and 5.0 ms following pulse initiation, during which time species within the plasma are subject to a mix of electron ionization, charge transfer, and Penning ionization; so many fragments can be obtained. The afterpeak regime can be found with a time gate of 5.2-5.8 ms,¹⁸ during this period, molecular ion information can be obtained, because the type of ionization is soft, similar to chemical ionization.

This chapter will focus on the study of the real time speciation of volatile organoselenium compounds (DMeSe and DMeDSe) by GC-GDToF. The unique information from each time regime can be gathered by gating the repeller pulse with respect to the GD pulse, for example, 0.4 ms for prepeak, and 4.4 ms for plateau and 5.6 ms for afterpeak. Thus elemental information can be obtained from prepeak spectra, structural information can be found from plateau spectra, and molecular information can be obtained from afterpeak spectra. The DMeSe and DMeDSe compounds will be separated by GC, and then introduced into the glow discharge chamber accordingly. Because the LabVIEW program was set up to record three spectra from three different

time-gates automatically, the chemical speciation will be achieved nearly in real time.

2.2 Experiment

2.2.1 Reagents

Analytical reagent grades of dimethyl diselenide 99% and dimethyl selenide were purchased from commercial suppliers (Alfa Aesar, Ward Hill, MA) and used without further purification. Sample solutions were made by mixing 2000 μl dimethyl diselenide and 3000 μl dimethyl selenide into a 20 ml pre-cleaned volatile analyte (VOA) sampling vial (Restek Corporation, Bellefonte, PA) using a 1000 μl Eppendorf micro pipette (Brinkmann Instruments, Inc., Westburg, NY). HPLC grade benzene and toluene (Fisher Scientific, Pittsburgh, PA) were used to optimize the instrument parameters. A 5 μl SGE removable needle syringe (Alltech Associates, Inc., Deerfield, IL) was used to inject 1 μl samples manually onto the GC column via a split/splitless injector.

2.2.2 Apparatus

Gas Chromatography:

A gas chromatograph (Model 3400, Varian Instrument, Walnut Creek, CA) with a split injector and a 30 m capillary column was used to separate the samples. The column

used was a 0.25 mm ID, 5% phenyl-95% methyl polysiloxane column purchased from (Agilent technology, Chicago, IL). During all experiments, ultra pure argon (Airgas, Randor, PA) was used as the carrier gas, which is also used as the working gas to produce the glow discharge plasma. The GC carrier gas flow was 2.8 ml/min. The split ratio of the split injector was 46.8:1. The split injector was operated at a split flow rate of 58.7 ml/min. Manual injection was used by drawing 1 μ l of sample into a 5 μ l syringe (SGE, Restek Corporation, Bellefonte, PA) from the 20 ml pre-cleaned volatile organic analyte sampling vial (Restek Corporation, Bellefonte, PA). The injector temperature and the column temperature were set as listed in Table 2.1. Upon exiting the GC oven, the terminal end of the capillary was introduced into a stainless steel tube (1 mm ID), that guided the GC capillary into the GD chamber. As shown in Figure 2.1, the steel tube is inserted into the glow discharge chamber through a Swagelok fitting on a double sided flange. An electrical heating tape was wrapped around the outside of the interface to keep that portion of the column at a temperature of 100°C. Figure 2.2 illustrates the positioning of the capillary: 2 mm in front and 0.5 mm to the side of the ion exit orifice. General GC operating conditions used in the experiment are listed in the Table 2.1.

Figure 2.1 The interface design between gas chromatography and glow discharge time of flight mass spectrometer

GC model	Varian 3400
Column	30 m×0.25 mm, 5% phenyl-95% Methyl polysiloxane
Split ratio	46.8:1
Carrier gas	Ar, 58.7 ml/min split flow rate

	Toluene	Benzene	Volatile Se
Injector port temperature	145°C	125°C	225 °C
Column temperature	115°C	100°C	40 °C, 4 min isothermal, then 15 °C min ⁻¹ to 120 °C, 5 min isothermal

Table 2.1 Gas chromatography general operating conditions

Pulsed Glow Discharge Source:

The glow discharge chamber was designed as a bellows system housing the plasma attached to the double-sided conflat flange within a six-way high vacuum stainless steel cross (MDC Vacuum Products Co., Hayward, CA). Side ports on the cross are equipped with a direct insertion probe inlet, auxiliary gas inlet, and capillary inlet. The direct insertion probe introduces a copper disk cathode into the glow discharge chamber to produce the plasma. The copper disk cathode is fabricated from a copper rod (SRM 855, NIST, Gaithersburg, MD). The distance between cathode and ion exit orifice can be adjusted by moving the direct insertion probe backward or forward. The capillary is introduced into the chamber and positioned between cathode and ion exit orifice, which is parallel to the DIP without touching the cathode and perpendicular to the ion exit orifice. Figure 2.2 illustrates in detail the design of the GD chamber. Stainless steel conflat flanges are used to fit the other remaining ports of the cross. The power supply system of plasma is a 13.56 MHz radio frequency (RF) generator (Model RF 10-s, RF Plasma Products, Inc., Marlton, NJ) equipped with an automatic matching network (Model AM-10, RF Plasma Product Inc., Marlton, NJ, USA). The RF power supply with the internal pulsing mode permits control of duty cycle, pulse width, and power level for the applied RF power pulse. Throughout the experiments, the operating power was set at 120 W with 25% duty cycle and the RF pulse width set at 5 ms. Ultra pure Ar gas (Airgas, Randor, PA) was used as discharge gas introduced into the glow discharge chamber through a metering valve. The pressure was monitored by a thermocouple pressure gauge

(Varian, Lexington, MA). The operation conditions of pulsed glow discharge are listed in Table 2.2.

Figure 2.2 Glow discharge chamber configuration

TOF Mass Spectrometer:

The instrument has already been described in detail previously.^{19,20} The time-of-flight mass spectrometer employed was a linear flight instrument (R.M.Jordan Co., Grass Valley, CA) with orthogonal sampling of the ion beam from the glow discharge source. Figure 2.3 is the GD-TOF MS system configuration. The ions formed are extracted into the time-of-flight acceleration region using a series of electrostatic lenses including a skimmer cone with a 1 mm sampling orifice. An added slit can narrow down the spatial distribution of ions moving through the skimmer. General operating conditions for the TOF mass spectrometer used in this experiment are presented in Table 2.2. Pulsed operation of the glow discharge is well suited to the time-of-flight mass spectrometer for the pulsed injection of a sample packet of ions into the 1 m flight tube. A digital delay generator (EG&G Princeton Applied Research, Princeton, NJ) synchronized with the RF power pulse is used to set an internal adjustable delay relative to the initial trigger which is positioned at the glow discharge power onset. This delay triggers the application of a 1 μ s wide positive potential pulse to the repeller, injecting an ion pack into the flight tube. The vacuum system included two roughing pumps and two turbo molecular pumps that evacuated the flight tube to an operating pressure of 10^{-6} Torr. The accelerated ions are directed through the stainless steel liner to a microchannel plate detector (Model C-701/25, R.M. Jordan Company Inc., Glass Vally, CA) using a pair of X and Y deflectors.

Figure 2.3 Pulsed glow discharge time-of-flight mass analyzer system

Glow Discharge

Discharge gas	Argon
Pressure	0.5 Torr
Operating power	120 W RF
Sampling Distance	5-25 mm
RF pulse duration	5 ms
RF pulse duty cycle	25 %

Time-of-flight

Flight path length	1 m
Ion lenses potential	
• Skimmer	-1079 V
• Extractor	0 V
• Accelerator/flight tube	-1670 V
• Deflector (x)	-1995 V
• Deflector (y)	-1620 V
• Repeller	+215 V; 1 μ s
• Detector	-1836 V
Vacuum conditions	
• Intermediate stage	10 ⁻⁵ Torr
• Flight tube	10 ⁻⁶ Torr

Table 2.2 Operating parameters used for the pulsed GD TOF-MS

Data Acquisition and Processing:

Figure 2.4 is a block diagram showing the time-gated data collection system. A digital delay generator synchronized the RF power pulse with the TOF repeller pulse. The DDG triggered the repeller pulse and the initiation of the signal detection system. The time gate was set respectively at 0.4 ms, 4.0 ms and 5.6 ms to obtain mass spectra from the prepeak, plateau, and afterpeak respectively. The mass spectrometry data was amplified and then collected by a 1-GHz oscilloscope (Lecroy 9370 M, Chestnut Ridge, NY). Spectra were averaged continuously (1:30). Data collected by the oscilloscope was transferred to a computer through a GPIB card that was controlled by acquisition software (LabVIEW 6.1, National Instruments, Houston, TX, USA) with a transfer rate of 120 data files/min (2 Hz). To acquire the summed ion chromatogram (SIC), an acquisition window was set over a certain m/z range. Figure 2.5 shows how the acquisition window was set to obtain a SIC from the plateau regime. The light blue shadowed area indicates the acquisition window and the intensity of each ion signal that appears in this window will be summed together. The summed intensity is then plotted as a function of elution time to form the summed ion chromatogram. The m/z range was changed to acquire summed ion chromatograms for different analytes as shown in Table 2.3. Another LabVIEW program was used to review the data acquired and translate the spectra to ASCII format. A Microsoft Excel 97 spreadsheet program was created to open the ASCII data and create the final mass spectrum.

Acquire window (SIC)	Toluene	Benzene	DMeDSe & DMeSe
	67-100 m/z	70-80 m/z	70-200 m/z
Prepeak spectra	acquired at 0.4 ms		
Plateau spectra	acquired at 4.0 ms		
Afterpeak spectra	acquired at 5.6 ms		
Average continuously	1:30		
Transfer rate	120 data files/min		

Table 2.3 Data acquisition parameters

Figure 2.4 Block diagram of the time-gated data acquisition system

Figure 2.5 Creation of a summed ion chromatogram

2.3. Results and Discussion

2.3.1 Selection of Experimental Parameters

GC Carrier Gas & Glow Discharge Gas Selection

Benzene and toluene were used to optimize some of the instrument parameters relating to the gas chromatograph coupled to glow discharge ToFMS. It was found that the potential energy of the selected noble discharge gas should relatively match the ionization potential of the target analyte when obtaining the intact molecular parent ion without considerable fragmentation is desired.¹⁵ Argon gas was chosen as the glow discharge gas because argon has metastable energies of 11.55 eV and 11.72 eV, which are close to the ionization potential of dimethyl selenide (8.4 eV), dimethyl diselenide (8.5 eV), Toluene (8.8 eV), and Benzene (9.24 eV).

Helium is most frequently chosen as the carrier gas for gas chromatography. However, if helium were used as the carrier gas in this experiment, the discharge gas would be a mixture of helium and argon. The presence of low concentrations (even below 10%) of contaminant gases affect Penning ionization and decrease molecular ion generation.^{15,21} Because the helium atom has a much higher ionization potential and concentration than the eluting compounds, the metastable argon atom population would decrease and ionization would be prevented. Therefore, in this experiment, ultrapure argon is chosen, as opposed to helium, as the gas chromatography carrier gas.

Discharge Pressure

Previous work in this group studied how glow discharge pressure affects molecular analysis.¹⁸ It is known that high pressure can cause severe collision induced dissociation, which results in extensive fragmentation. Thus it is hard to get molecular and structural information under high pressure. Also, measured ion intensity decreases at high pressure. Meanwhile, under low glow discharge pressures, the plasma is not very stable. In Lei Li's work, an optimal glow discharge pressure in the range of 0.2-0.6 Torr is suggested. A discharge pressure of 0.5 Torr was chosen in the following study.

Discharge Power

While the operating power does not affect the internal energy distribution and change the spectrum shape, it can change the signal intensity. Higher operating power results in higher signal intensity, which increases analytical sensitivity. On the other hand, operating at higher powers can impair plasma stability. In this experiment, 120 W RF power was used to get satisfactory signal and plasma stability.

Data Acquisition Rate, Glow Discharge Pulse Rate, and Duty Cycle

The data acquisition rate is very important in this study because of the introduction of a transient vapor. The half peak width of the chromatographic peaks was found to last around 30 s. The manual data collection method could not be used in this

study because it takes about 1 min to collect one data point, which is too slow to catch the dynamic signal. Typically the crest of the chromatographic peak is selected to get the strongest mass spectrum of the separated compound, which makes a faster data collection rate required. In this experiment, the amount of spectra being acquired was limited to 120 spectra/ minute (2 Hz).

The glow discharge pulse was applied with a 25% duty cycle, which translates to 5 ms pulse on and 15 ms pulse off,. The relatively long pulse off time ensures enough time for the cathode to cool down and not overheated while letting ion species resulting from the previous pulse disappear and not affect the next cycle.

Background Cu Spectra

Background Cu spectra from the prepeak, plateau, and afterpeak are shown in Fig 2.9. The prepeak spectrum shows mostly background signal from the plasma environment, including the discharge gas, argon, and other contaminate gases. It shows signal resulting from water residue at 15-20 m/z, N₂ at 29 m/z and O₂ at 32 m/z. The argon glow discharge gas, Ar⁺, is at 40 m/z. The Cu isotope signal, appearing at 63 and 65 m/z, is observed in the prepeak spectrum which was taken at 0.4 ms following power onset. This indicates that the copper cathode has had sufficient time for sputtering, diffusion into the glow discharge, and subsequent ionization in this situation. Inclusion of the cathodic material in the prepeak spectrum may also have been caused by a short

distance between the cathode and the ion exit orifice. Thus the diffusion will happen quickly and the copper signal can be detected.

The plateau spectrum of Cu is similar to the prepeak except the signal of copper increases greatly. This is a result of the increase in ionization processes which include electron impact ionization, charge exchange and Penning ionization. The ion product is the mixture and competition of all of these ionization processes.

It is very interesting that in the afterpeak spectrum of Cu, the background contaminates and the discharge gas signal disappears while the copper signal dominates the spectrum. This can be attributed to the cessation of electron impact ionization with the termination of the applied power. Penning ionization is the main ionization mechanism at this time and thus increases the sample cathode signal intensity.

(a) Prepeak

(b) Plateau

(c) Afterpeak

Figure 2.9 Mass spectra of Cu obtained within the (a) prepeak, (b) plateau, and (c) afterpeak regime

2.3.2 Chromatographic Separation

Summed Ion Chromatography Data Acquisition System Set and Sample Introduction Rate Study Using Toluene as a Sample Molecule

An example using toluene can illustrate the variety and amount of information obtained from a single experiment by the plots and spectra given out in Figure 2.6. In this study, toluene is also used to study the gas flow rate from the gas chromatograph to the glow discharge chamber. The sample introduction flow rate is very important and needs to be controlled carefully. It is found that a too slow sample introduction rate results in low analyte ion signal intensity, while too much sample introduced into the plasma within a short time can quench the plasma and cause complete loss of the signal. Toluene sample injections were performed using 1 μl of solution. The split injector was used to remove excess solution and thereby reduce plasma quenching. In this experiment, the split injector was operated at a temperature of 145 $^{\circ}\text{C}$, with an optimized split flow rate of 58.7 ml/min, which makes the split ratio 46.8:1. The column temperature was set at 115 $^{\circ}\text{C}$ and the column pressure at 22 psi.

The digital delay generator was set at 4.4 ms to watch the plateau spectra, because the plateau regime has the strongest total signal intensity. The ion chromatogram was based on ion fragmentation data taken during the plateau time regime using a range of 67-100 m/z, which excludes background signal from the argon discharge gas and copper cathode and includes the molecular ion for toluene. The summed intensity value was

plotted as a function of the elution time to provide a means for indexing the digitized oscilloscope traces or specific mass spectrum with the eluting time.

The ion chromatograph in Figure 2.6 shows that at 3 minutes the toluene sample starts its elution. Several typical toluene spectra were selected for Figure 2.7 to illustrate. Data point 1 which is at 1 min was chosen to show the background signal, in which Ar^+ appears at 40 m/z and the Cu^+ isotopes at 63 and 65 m/z with an isotope ratio of 2:1. Data points 2 and 3 are collected within the elution time of toluene. Spectrum 3 was acquired at the crest of the toluene peak while spectrum 2 was collected just prior to the crest. In both spectra, the toluene peak appears at m/z 92. Comparing these two spectra, it was found that the background signal (argon gas and copper) decreased and the intensity of the toluene signal increased with the increase in chromatogram signal intensity. Spectra 4 and 5 are collected after toluene elutes out. In these two spectra, there is no toluene signal and the background signal returns. In spectrum 4, the copper signal is absent, probably because the plasma is somewhat quenched by the eluted sample. Later, the glow discharge plasma returns and the Cu signal is observed in spectrum 5. In Figure 2.8, a NIST standard electron ionization mass spectrum of toluene collected at 70 eV is included together with the GD-TOF MS plateau spectrum 3. By comparing these two spectra, it is found that the resulting fragmentation patterns are similar in both spectra.

Figure 2.6 Toluene summed ion chromatogram collected during the GD plateau regime

1

2

3

4

5

Figure 2.7 Mass spectra collected at various elution times

3

NIST

Figure 2.8 Toluene plateau mass spectrum & NIST standard spectrum

2.3.3 Temporal Regime Evaluation Using Benzene as a Sample Molecule

Benzene is used to evaluate the different temporal regimes of the glow discharge and the LabVIEW program's ability to collect the 3 different sets of data. A 1 μ l benzene solution was injected into the GC column. The column temperature was 100 °C and the injector port temperature was set at 125 °C. Figure 2.10 is the ion chromatogram constructed by monitoring the ion peak intensities over 70-80 m/z during the plateau regime as a function of elution time. From the summed ion chromatogram, benzene elutes at 1.5 min.

The ion chromatogram looks choppy and noisy; it may be caused by the LabVIEW program or the interface between the GC and the glow discharge chamber. Although a heating tape is used to wrap the outside of interface, the part of the stainless steel capillary inside the GD chamber is still at a low temperature, possibly allowing for condensation of the sample inside the capillary and hence a tail or noisy signal is produced.

Figure 2.11 shows the spectra collected at different delay times. In the prepeak spectrum, the data is collected at 0.4 ms after the power initiation. A high energy electron population is formed and the argon discharge gas breaks down. Some residual or contaminant gas in the glow discharge chamber is ionized too. All of these gas species are ionized by electron impact. Background signal from contaminant gases appear in the range from m/z 10 to 30. Signal from the discharge gas, argon, appears at 40 m/z.

Looking at the spectrum, there is no signal from the glow discharge copper cathode and sample benzene at this time.

The plateau spectrum shown in Figure 2.11 was collected at a delay time of 4.4 ms from the start of the pulse cycle. At this time, the charged species increased and electron impact ionization is no longer the dominant ionization mechanism. The ionization within the plasma becomes a mixture of competing ionization mechanisms and recombination processes. And the signal intensity of all species reaches a plateau status. Previous work using volatile organic compounds as samples found that spectra collected during this time resembled EI spectra obtained with electron kinetic energies of 70 eV.¹⁸ In the plateau spectrum, an extensive fragmentation signal can be obtained. As seen in Fig 2.12, compared to a standard NIST spectrum collected at 70 eV, all the peaks in the plateau spectrum are correlated to the fragmentation signals in the NIST standard spectrum. This illustrates that at this time the plasma functions in a similar mode as the continuous glow discharge.

As for the afterpeak spectrum, data is collected at 5.6 ms according to the digital delay generator setting, which is 0.6 ms after the GD power terminates. The signal of the background or discharge gas decreases and the analyte signal for benzene becomes relatively more intense than spectra collected at other time regimes. This is due to the large amount of argon metastable atoms produced with the main ionization mechanism being Penning ionization in the afterpeak regime.

Figure 2.10 Summed ion chromatography at plateau regime 4.4 ms into the pulse

(a) Prepeak 0.4 ms

(b) Plateau 4.4 ms

(c) Afterpeak 5.6 ms

Figure 2.11 Mass spectra of benzene obtained within the (a) prepeak, (b) plateau, and (c) afterpeak regime

Figure 2.12 Mass spectrum of benzene obtained within the plateau regime and NIST electron impact (70 eV) reference spectrum

2.3.4 Separation of DMeSe and DMeDSe

Dimethyl selenide (DMeSe) and dimethyl diselenide (DMeDSe) are separated by GC and detected with GD-TOF-MS. To decrease the background signal and clean up the mass spectra, ultra pure argon was used as the GC carrier gas in addition to being used as the glow discharge gas. In this experiment a 1 μ l sample was injected into the GC. The split ratio of 46:1 was used to control the flow rate and the amount of sample introduced into the glow discharge chamber. Too much sample introduced into the chamber could quench the plasma. The GC column temperature was programmed in order to decrease separation time and improve separation efficiency because the difference between the boiling points of DMeSe (56-58 °C) and DMeDSe (155-157 °C) is very large. Fig 2.13 is the summed ion chromatogram for both compounds, in which the summed window set at m/z 70-200. Fig 2.5 shows the window set in detail. The summed intensity value of the ions within the window was plotted as a function of time to form the summed ion chromatogram. The ion chromatogram can be used as an index to load mass spectra from the three different time regimes and select the best mass spectrum for each sample. In Fig 2.13 the summed ion chromatogram shows that the first compound eluted at 2.5 min, while the second compound eluted at 7 min.

Figure 2.13 The index summed ion chromatography of DMeSe and DMeDSe

2.3.5 Mass Spectra of DMeSe

Using the SIC as an index, the prepeak, plateau and afterpeak mass spectra of DMeSe can be reviewed and analyzed following the data collection process. The mass spectra change a lot from the beginning to the end of the elution. When replaying the collected spectra according to elution time using the LabVIEW program, it is obvious that with the elution of DMeSe, the background signal (for example Cu, Ar) decreases and the signal of DMeSe increases and becomes most intense at the top of the first ion chromatography peak. Time gated detection of the full mass spectrum during the specific ionization regime makes it possible to collect elemental, structural, and molecular weight information.¹⁵ The task can be performed in real time by a time-of-flight mass spectrometer with the eluting analyte stream.²² In the following discussion, one data point is chosen from each chromatogram as an index which represents three independent mass spectra collected for each eluting species.

To illustrate the species present and plasma conditions before the eluting compound enters the glow discharge cell, background spectra as shown in Fig 2.14 is taken at time A in the chromatogram as shown in Fig 2.13.

(a) Prepeak

(b) Plateau

(c) Afterpeak

Figure 2.14 Glow discharge background mass spectra obtained within the (a) prepeak, (b) plateau, and (c) afterpeak regime

Fragmentation pattern: The mass spectrum for diethyl selenide and diethyl diselenide has been reported by Meijiaa et al.²³ According to this paper, the fragmentation pattern of dimethyl diselenide is illustrated as the following scheme.

Prepeak: A prepeak mass spectrum of DMeSe is shown in Fig 2.15. At this time, the high electron temperatures within the glow discharge plasma cause the molecule to completely atomize and ionize. Therefore, intensive fragmentation, abundant atomic ions and a small abundance of fragment ions can be observed from mass spectra collected in this time regime and the elemental composition of the eluted analyte can be revealed. As expected, background contaminant gas signals of H_3O^+ (19 m/z) and of the glow discharge gas Ar^+ (40 m/z), appeared in the prepeak spectrum. A small peak of Cu^+ (63 and 65 m/z) can be seen in the prepeak spectrum which is unusual. It may be that the time gate, selected at 0.4 ms, was triggered too far into the pulse cycle or the cathode was positioned too close to the ion extraction port; therefore allowing enough time and a short enough distance for the Cu ions to be formed, diffused, extracted and detected. The selenium atomic ion, Se^+ , is seen in the mass spectrum at m/z 80, although it may be overlapped by argon dimer ions, Ar_2^+ . Considering the argon dimer ion does not appear at m/z 80 in the background spectrum, m/z 80 should be attributable to selenium atomic ions only. Additionally, the ratio of the peaks correspond to the isotope distribution of selenium, 50% ^{80}Se and 24% ^{78}Se . Also HSe^+ and H_2Se^+ ions appear at 81 and 82 m/z respectively. The fragment ions CH_3SeH^+ and CH_3Se^+ appear at m/z 96 and 95 respectively. The DMeSe molecular ion can be seen at 110 m/z. But compared to other

peaks, it is not very strong. This is because the molecular ion still has enough internal energy to dissociate.

Plateau: Fig 2.16 is a plateau mass spectrum of DMeSe selected at the crest of the chromatogram peak because the sample ion intensity is largest at this point. From the mass spectrum, we can see the molecular ion of $\text{CH}_3\text{SeCH}_3^+$ at m/z 110, CH_3Se^+ and CH_3SeH^+ at m/z 95 and 95, Se, HSe^+ and H_2Se^+ at m/z 80-82, and CH_2^+ and CH_3^+ at m/z 14 and 15. The peak at m/z 25 may be the chemical reaction product of the free radical - CH_2 and - CH_3 , because self-chemical ionization can occur in addition to the well established plasma ionization mechanisms. Compared to the standard mass spectrum of dimethyl selenide from NIST, the plateau mass spectrum seems very similar to the standard mass spectrum which is done using 70 eV EI. Small differences can be attributable to Penning ionization and charge exchange. This proves that the tunable RF pulsed glow discharge is a versatile ionization source. During the plateau time regime, a lot of fragmentation appears because the mass spectrum is a result of the mixing of electron impact, charge exchange and Penning ionization. Thus the plateau mass spectrum gives us structural information.

Afterpeak: An afterpeak mass spectrum of dimethyl selenide is shown in Fig 2.15. In this spectrum, the molecular ion of dimethyl selenide appears at 110 m/z . Compared to the plateau mass spectrum, the afterpeak mass spectrum is simpler and cleaner, if not considering the background signal of H_3O^+ (18 m/z) and Ar^+ (40 m/z). The peak at 80-82 m/z (Se, HSe^+ and H_2Se^+) disappeared and the peak at 95-96 m/z (CH_3Se^+

and CH_3SeH^+) decreased in intensity, while the molecular ion at 110 m/z increased dramatically and became a predominant signal, because Penning ionization is the main process during the afterpeak regime in which the relaxed plasma energy is about 9 eV. Thus fewer fragments are present and their intensity is much smaller.

Prepeak

Afterpeak

Figure 2.15 Representative mass spectra of dimethyl selenide obtained within the prepeak and afterpeak regime

Plateau

NIST

NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

Figure 2.16 Representative plateau mass spectrum and NIST electron impact (70 eV)

reference spectrum of dimethyl selenide

2.3.6 Mass Spectra of DMeDSe:

Similar to dimethyl selenide, the mass spectra of dimethyl diselenide were selected from the crest of the ion chromatogram and show the differences in information attainable from the prepeak, plateau and afterpeak of the GD pulse.

Fragmentation pattern: The fragmentation pattern of DMeDSe can be expected as following.²⁵

Prepeak: The spectrum of DMeDSe collected during the prepeak regime is shown in Fig 2.17. The elemental Se peak appears at 80 m/z and the intensity of the peak is relatively bigger than other species. SeCH₃ fragments can be seen at 95 m/z. Se-Se fragments were found at at 160 m/z. The ion of the discharge gas argon, Ar⁺, appears at m/z 40. The molecular ion of DMeDSe was not detected. This proves again that during the prepeak time regime, the plasma is highly energetic making it easy to obtain elemental ions, but difficult to obtain the molecular ion.

Plateau: The plateau mass spectrum of DMeDSe in Fig 2.18 should show a similar spectrum to the 70 eV EI mass spectrum from NIST. In the NIST standard

spectrum, the following peaks are detected: Se-Se peaks at 160 m/z, HSeSeH at 162 m/z, SeSeCH₃ at 175 and HSeSeCH₃ at 176 m/z. The molecular ion of CH₃Se-SeCH₃ appears at 190 m/z. These higher mass species do not appear in the plateau mass spectrum for DMeDSe. In the plateau spectrum, an intense SeCH₃ peak can be observed at 95 m/z, because 1 mol of CH₃Se-SeCH₃ can be broken into 2 moles of SeCH₃. Some small peaks of CH₂ and CH₃ are present at 14 and 15 m/z too. All of these peaks provide information about the molecular structure.

Afterpeak: Fig 2.17 shows the afterpeak regime spectrum, from which molecular identification should be readily achieved. The predominance of the DMeDSe molecular ion peak is expected to be seen due to the plasma energy during this regime is lower than other fragmentation energies. Following cessation of the GD pulse, the energy of the plasma is decreased, thus not as many fragments appear in the afterpeak spectrum as in the plateau spectrum.

Unfortunately, from the spectra, especially the afterpeak spectrum, no molecular ion of dimethyl diselenide is observed in this experiment. This is most likely caused by the following factors. First, the heating tape covering the interface between the gas chromatograph and mass spectrometer was set at 100 °C, which is lower than the dimethyl diselenide boiling point of 155-157 °C. The temperature of the transfer line below the boiling point temperature may have caused the dimethyl diselenide compound to remain in the GC column. Secondly, there is a section of GC column in the glow discharge chamber which can't be heated. Under these conditions, the dimethyl

diselenide may have cooled down and re-condensed before entering the glow discharge chamber and mass spectrometer. These two factors may also contribute to the low quality signal of the spectra of dimethyl diselenide.

Prepeak

Afterpeak

Figure 2.17 Mass spectra of dimethyl diselenide obtained within the prepeak and afterpeak regime

Plateau

Figure 2.18 Representative plateau mass spectrum and NIST electron impact (70 eV) reference spectrum of dimethyl diselenide

2.4. Conclusions

In this chapter, GC-pulsed GD ToF was examined for its potential to permit real time chemical speciation of DMeSe and DMeDSe. Pulsed glow discharge is a versatile ion source and very suitable for ToF MS. By gating the repeller pulse with respect to the GD pulse, spectra from 3 unique time regimes, the prepeak, plateau, and afterpeak, can be obtained. Spectra collected during the prepeak can give elemental composition, spectra from the plateau can give structural fragments, and afterpeak spectra can provide molecular weight information. All of this information can be obtained quickly within a transient period of usually a few microseconds. Because of its speed and ease of operation, the pulsed glow discharge time-of-flight can be used as an on-line and real-time detector when coupled to GC. The compounds within the sample were separated by GC, introduced into the glow discharge chamber, and then identified by TOF mass spectrometry. After recording and analyzing the data using a home-made LabVIEW program, real time chemical speciation of DMeSe was realized, but the ability to determine DMeDSe was limited by the available equipment.

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Chapter 3

Direct Chromium Speciation in Solid State Materials - A GDMS

Approach

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Abstract

Among the various elemental mass spectrometry techniques, glow discharge mass spectrometry is recognized for its ability to provide direct determination of trace elements present in solid state samples. In the present work, a pulsed glow discharge time of flight mass spectrometry method is developed for the direct speciation of chromium in solid state samples. The millisecond pulsed glow discharge with radio frequency power is a versatile ion source that provides elemental, structural and molecular information. Careful tuning of the operating parameters yields the plasma chemistry that favors cluster ion formation. Cluster ions unique to specific species permit differentiation between the trivalent and hexavalent forms of chromium, (CrIII) and (CrVI) respectively, in chromium oxide samples. Specifically, signals at 104 and 120 m/z corresponding to the Cr_2^+ and Cr_2O^+ cluster ions are indicative of the presence of Cr(III) in the sample, whereas signal at 100 m/z corresponding to the CrO_3^+ cluster ion arises from the presence of Cr(VI). The impact of glow discharge operating conditions on the appearance of these characteristic cluster ions is discussed.

3.1. Introduction

In analytical chemistry, a trace element is usually defined as an element with an average concentration of less than 100 ppm in a given sample. The term dates back to the early 20th century, when scientists were able to detect minute amounts of several elements in living organisms, often describing them as being present in "traces" or "trace amounts".¹ Throughout the next half century, all efforts to analyze trace elements were focused on total concentrations.² Elemental speciation didn't come to the forefront of the scientific community until the late 1950's and early 1960's with the methyl mercury poisoning epidemic of the Japanese residents near Minamata Bay. Subsequent anthropogenic pollution incidents, such as oyster extinctions in Arachon Bay, France due to tributyltin antifouling paints and globalized lead pollution from antiknock agents in gasoline, further demonstrated the need for analytical methodologies to detect and identify specific chemical forms of trace elements.³

Elemental speciation seeks to identify, characterize, and quantify the defined species, forms, or phases of an element present in a given sample and its distribution.⁴ The importance of elemental speciation lies in the fact that environmental changes influence the behavior of both essential and toxic elements through alterations of the forms in which they occur. These forms, including oxidation state and the associated complex or molecular form, profoundly impact the toxicity, bioavailability, metabolism, transport, uptake, and distribution of the element.⁵ Chromium is just such an example, the toxicity of which is oxidation state dependent. Whereas the trivalent species of chromium

(CrIII) is an essential nutrient needed in ultra-trace quantities, the hexavalent species (CrVI) is a known carcinogen and is toxic to humans. By understanding the most important forms of an element and the transformation processes between those forms, one can more accurately predict their environmental impact. It is for this reason that the relevance of speciation science spans many different scientific backgrounds: specialists in chemistry, biology, geology, physics, nutrition, and medicine all have a need for this kind of information.⁵

A speciation study of a given material might include the determination and quantification of the elements present, as well as identification of the chemical nature or molecular form of each species. Such analysis typically requires a plethora of instrumental techniques, sample preparation procedures, and chemical analysis methods.⁶ The most common approach to elemental speciation is the utilization of chromatographic separation methods coupled with elemental or molecular characterization techniques such as atomic spectroscopy or mass spectrometry.⁷ However, as Marcus states “the greatest level of specificity comes from methods that allow the unambiguous identification of a complete analyte entity” including molecular weight as well as “selective information related to molecular structure (i.e., fragmentation patterns)”.⁸

In recent years, mass spectrometry (MS) has proven to be the best detection choice for speciation analysis because it provides both the sensitivity and selectivity needed to assess the molecular, structural, or elemental composition of a given analyte. Nevertheless, the type of elucidation achieved by MS is largely contingent on the

ionization method used. “Hard” ionization methods like inductively coupled plasma (ICP) provide information regarding the elemental composition, whereas methods like electrospray ionization (ESI), a “soft” ionization technique, allow for the detection of intact molecular ions. As a result, to achieve a complete characterization of a given sample, one must interface among multiple detection methods inevitably increasing the time, cost, sample size and operator skill needed to conduct the analysis.⁷

Classic chromatographic and ‘wet chemistry’ techniques utilized in elemental speciation further complicate the analysis. Because these techniques require liquid samples, many complicated pretreatment procedures, such as extraction, preconcentration, or derivatization are needed. These methods not only lend to additional analysis duration and solvent cost, but also open the possibility for oxidation or reduction reactions to occur, thereby altering the speciation of the original sample.⁹ For the analysis of geological samples where the specificity of a particular elemental valency is of great concern, it is often necessary to avoid such modifications and preserve the sample in its natural condition, thus making liquid techniques obsolete.³

It is the combination of these two pressing needs, a mass spectrometric ionization source that can provide concurrent elemental, structural, and molecular information and the necessity for a direct solid sampling technique, that has led our group to investigate the use of a glow discharge time of flight mass spectrometry method for the direct speciation of chromium in solid state samples. Glow discharge (GD) plasmas are “steady-state but highly heterogeneous plasmas with a number of dynamic processes occurring

simultaneously”.⁶ The atomization of an analyte in a GD ion source arises through cathodic sputtering, in which ionized discharge gas atoms, created by the breakdown of the discharge support gas, are accelerated toward the cathode where they bombard the surface and “knock off” sample atoms. Once atomized, the sputtered analyte atoms can become excited or ionized in the surrounding plasma via interactions with numerous energetic species such as fast electrons, excited and metastable atoms, and ions generated in plasma sustaining processes. Each species transfers energy to analyte molecules through a characteristic ionization process that can excite them within a particular energy range. These processes include electron ionization, charge transfer, and Penning ionization.⁷

When operated in the pulsed mode, spatial and temporal separation of the different ionization mechanisms becomes possible through the creation of three distinct time regimes during each on/off cycle: a prepeak dominated by electron ionization, an afterpeak dominated by Penning ionization, and a steady-state plateau which arises from a mixture of electron impact, charge transfer, and Penning ionizations.¹⁰ As a consequence, analyte molecules are exposed to a series of transient ionization periods within each pulse cycle that range from “hard” to “soft”, allowing for a highly tunable ion source.⁷ By coupling a pulsed GD plasma ion source with time-of-flight mass spectrometry (Pulsed-GDMS) and selecting a particular time regime/plasma chemistry, elemental and/or molecular information may be obtained regarding a sample’s composition.

The use of GD plasma is now well established for the direct determination of trace elements in solid state samples, including geological materials.^{11, 12, 13} Previous research from this lab has also demonstrated the ability of this technique to be modified by time gating to permit chemical speciation of volatile organic and organometallic compounds.^{6,7,10} In the present work, a Pulsed-GDMS method for the direct speciation of chromium in solid state samples is presented. Based on similar work conducted by Aubriet et al. utilizing secondary ion mass spectrometry (SIMS),^{9,14} unique mass spectral features have been found that permit differentiation between the trivalent and hexavalent forms of chromium, (CrIII) and (CrVI) respectively, in chromium oxide samples.

3.2. Experimental

The pulsed glow discharge mass spectrometry system employed in these investigations, Figure 3.1, consisted of the glow discharge ion source and chamber into which the sample materials were introduced, a linear time-of-flight (TOF) oriented orthogonally to the glow discharge ion beam, and associated electronics as described below. Experimental conditions can be found in Table 3.1.

Table 3.1. TOF-MS operating parameters	
Glow discharge	
Pressure	0.3-0.4 Torr
Operating power	100-130 W
Pulse duration	5 ms
Duty cycle	25%
Sampling distance	5-9 mm
Time-of-Flight	
Flight path length	1 m
Ion lenses potential	
Skimmer	-353V
Accelerator (A2), Flight Tube, X2, Y2	-1535 V
Deflector (X1)	-1800 V
Deflector (Y1)	-1549 V
Repeller (A1)	+250 V; 1 μ s
Detector	-1850 V

Figure 3.1. Schematic of the GD-TOFMS Instrument (refer to Table 3.1 for component descriptions).

3.2.1 Pulsed Glow Discharge Plasma Device

A 13.56 MHz radio frequency (rf) generator coupled with an automatic matching network (RF Plasma Product Inc., Marlton, NJ) was used to power the GD plasma. The internal pulsing mode of the rf power supply system permits control of applied power, pulse width, and duty cycle. A 5 ms pulse width with a 25% duty cycle was maintained throughout the experiments while the operating power was varied. The argon discharge support gas (ultra pure, Airgas, Randor, PA) was introduced through a metering valve to control the gas pressure which was monitored by a thermocouple pressure gauge (Varian, Lexington, MA).

3.2.2 Chromium Sample Cathode Production

Analytical reagent grades of chromium (III) oxide (Cr_2O_3) and chromium (VI) oxide (CrO_3) were purchased from commercial suppliers (J.T. Baker Chemical Co., Phillipsburg, N.J. and Alfa Aesar, Ward Hill, M.A. respectively). Because the chromium oxide samples do not form sturdy disk samples when pressed, they were mixed with spectroscopic grade silver or graphite powders (Alfa Aesar, Ward Hill, M.A. and Bay Carbon, Bay City, M.I. respectively). The silver matrix adds stability and makes the resulting pellets more conductive. The samples were prepared according to methods developed by this group.^{14,15} All constituent powders were dried overnight at 90 °C and stored in a desiccator until needed. Sample weights of between 1 to 2 g were prepared to yield the desired % weight compositions. The resulting powder mixture was then

homogenized in a ball-in-vial mixer (Wig-L-Bug, SPEX, Edison, N.J.) for 3 minutes. Approximately 160 mg of powder was compacted in a die assembly constructed in this department's machine shop under 4,000 lbs of pressure for 30 minutes. The resulting disk-shaped sample pellets were 5 mm in diameter and 4.5 mm in height.

3.2.3 Time-of-Flight Mass Spectrometer

Instrumentation: The mass spectrometer employed in this study was a linear TOF instrument (R.M. Jordan Co., Grass Valley CA) oriented orthogonally to the glow discharge ion beam. A six-way, high vacuum cross (MDC Vacuum Products Co., Hayward, CA) served as the GD chamber. Plasmas were generated using a direct insertion probe (DIP) onto which the disk-shaped sample cathodes, 5mm in diameter and 4.5 mm in height, were mounted (Figure 3.2). The DIP allows for axial movement inside the GD chamber enabling TOF sampling at different distances from the cathode surface (Figure 3.3). Using a nonconducting MACOR[®] shield (Accuratus, Washington, N.J.), constant cathode surface area and current density were maintained allowing only the face of the sample disk to be exposed to discharge sputtering. Further information on the design of this instrumentation can be found in previous papers published by this group.¹⁶

Figure 3.2. Schematic of the pellet holder used for mounting compressed sample pellets to the DIP.

Figure 3.3. Schematic of the GD ion source.

Data acquisition: A digital delay generator (DDG) (EG&G Princeton Applied Research, Princeton, NJ) in synchronization with the rf power pulse was used to trigger an ion extraction pulse to the TOF repeller thereby initiating the signal detection system. The DDG allows for time-gated detection with which mass spectra can be obtained at selected temporal intervals within the power pulse sequence (Figure 3.4). In this study, plateau and afterpeak spectra were collected between 4.8 ms and 5.3 ms from the pulse initiation. The mass spectrometric data was amplified and fed into a 1-GHz oscilloscope (Lecroy 9370M, Chestnut Ridge, NY) for collection. The spectra were averaged continuously at 1:1023 and transferred to the computer through a GPIB card where a macro tool was used to open the ASCII data in Microsoft Excel and produce the corresponding mass spectrum.

Figure 3.4. Schematic of the time-gated detection and data acquisition system for the TOFMS instrument. The digital delay generator (DDG) allows the trigger delay time (Δ) to be adjusted relative to the rf power onset.

3.3. Results and Discussion

3.3.1 Evaluation of Temporal Regimes

The majority of analytical glow discharge (GD) plasmas operate in a continuous power mode, generating steady-state analytical signals. When operated in a modulated or pulsed power mode, several unique characteristics are imparted to the plasma. These characteristics contribute to significant analytical advantages for pulsed GD plasmas over their continuous counterparts. First, because each “power-on” period is followed by a much longer “power-off” period allowing time for the cathode to cool, higher instantaneous power can be applied to the plasma to enhance sputtering, excitation, and ionization while preventing problems associated with sample overheating. Second, pulsed operation of the plasma enables temporal discrimination between analyte signal intensities and those of the discharge gas and background contaminants through the creation of three distinct time regimes, the prepeak, plateau, and afterpeak.¹⁷ Within each pulse cycle analyte molecules are exposed to a series of transient ionization periods: a prepeak dominated by electron ionization, an afterpeak dominated by Penning ionization, and a steady-state plateau which arises from a mixture of electron impact, charge transfer, and Penning ionizations.⁷ Such temporal discrimination allows for a highly tunable ion source offering windows of ionization that range from “hard” to “soft.” In the present study, it is the unique plasma chemistry of the afterpeak, the period immediately following the discharge power termination during which a large population of metastable argon species is created, that is of greatest interest.

Upon power termination, high-energy electrons rapidly lose kinetic energy through collisional processes in the GD chamber. Although these thermalized electrons are no longer sufficiently energetic enough to ionize gas-phase species, they can recombine with argon ions to form energetic metastable atoms.¹⁷ Metastable atoms efficiently ionize sputtered analyte atoms or molecules of lower ionization potentials through a process called Penning Ionization. During this process, collisions between metastable and analyte atoms result in the transfer of the metastable atom's potential energy, 11.55 and 11.62 eV for metastable argon atoms, to form an analyte ion and a ground state argon atom. Because Penning ionization is limited by the relatively low potential energies of the metastable argon atoms, molecular fragmentation is inhibited and thus the afterpeak exhibits enhanced signals for the molecular ions sputtered from the analyte material.⁶

Temporal comparisons were made between a pure silver pellet and a mixed pellet with 20% hexavalent chromium oxide (CrO_3) and 80% silver by weight (Figures 3.5 and 3.6). In each case, the GD plasma was operated at 120 W rf power and 0.32 torr argon discharge gas with the DIP positioned such that the cathode was 9 mm from the sampling orifice. Time resolved mass spectra were collected within each region of the pulse cycle for both pellets: prepeak (0.3 and 0.4 ms), plateau (4.9 ms), and afterpeak (5.1 ms).

Prepeak: Just after the onset of power, 0.3 and 0.4 ms into the pulse, electron ionization dominates as electrons are accelerated away from the cathode and interact with the discharge gas. At this time, the argon ion profile maximizes. Minimal

signal contributions are obtained from the sample species, silver and chromium, due to delays in analyte sputtering and diffusion into the negative glow region of the plasma.

Plateau: At approximately 1 ms into the pulse cycle and until power termination, the plasma reaches pseudo steady-state conditions. In this temporal region, ionization mechanisms equilibrate into a mixture of electron impact, charge transfer, and Penning ionizations. Mass spectra collected in this region tend to be highly fragmented, yielding structural information about the analyte. Plateau mass spectra were obtained at 4.9 ms into the pulse cycle. Signal contributions from both the argon discharge gas and cathode material are present. For the mixed chromium (VI) oxide and silver pellet, steady-state signals were obtained for the ions of Cr, CrOH, CrO₂H, and the isotopes of Ag (m/z 52, 69, 85, 107, and 109 respectively).

Afterpeak: At 0.1 ms after power termination (5.1 ms into the pulse cycle), analyte ion signals maximize while the intensities of discharge species and background contaminants wane. As stated earlier, this temporal region is dominated by Penning ionization through a large population of metastable argon ions. For the pure silver pellet, the 107 and 109 masses maximize and saturate the detector. The silver dimer (m/z 214) and water-silver complexes (m/z 125 and 127) can also be seen. For the mixed chromium (VI) oxide and silver pellet, the ion signal intensities for Cr, CrO, CrOH, CrO₂ and CrO₂H increase (m/z 52, 68, 69, 84, and 85 respectively) and the parent ion appears (CrO₃H, m/z 101).

Because this project desires the direct speciation of solid state samples to permit differentiation between the trivalent and hexavalent forms of chromium, the afterpeak time regime was chosen as the most analytically favorable for chromium cluster ion formation. All further mass spectra for chromium oxide and silver pellets were obtained at 5.1 ms. For the mixed pellets of chromium oxide and graphite, 5.3 ms was found to give the most intense analyte peaks.

Figure 3.5. Time resolved mass spectra of pure silver during the prepeak (0.3 ms and 0.4 ms), plateau (4.9 ms), and afterpeak (5.1 ms). Discharge pressure 0.32 torr, operating power 120 W, and sampling distance 9 mm.

Figure 3.6. Time resolved mass spectra of 20% chromium (VI) oxide and silver pellet during the prepeak (0.3 ms and 0.4 ms), plateau (4.9 ms), and afterpeak (5.1 ms). Discharge pressure 0.32 torr, operating power 120 W, and sampling distance 9 mm.

3.3.2 Evaluation of Operating Parameters

One can significantly affect excitation and ionization processes within the GD by controlling the plasma operating parameters. Careful adjustment of the applied power or discharge pressure makes it possible to selectively enhance a particular ionization mechanism thus providing additional tuning capabilities for the optimization of a given analyte signal.^{7,10} The operating pressure controls the collisional environment of the GD plasma, whereas the applied potential defines the kinetic energy that can be obtained by charged species in the plasma.¹⁵ Because excitation and ionization processes within pulsed GD plasmas show spatial heterogeneity over the pulse cycle, further tuning capabilities can be gained via careful selection of the plasma sampling region. Studies of discharge pressure, operating power, and sampling distance were conducted to favor the formation of chromium cluster ions in the plasma (Figures 3.7, 3.8, and 3.9 respectively). The optimal settings can be found in Table 3.2.

Discharge Pressure: The discharge pressure determines the mean free path and collision frequency of ions and atoms in the plasma. Figure 3.7 shows the effects of discharge pressure on the afterpeak mass spectra of a pellet mixed with 30% trivalent chromium oxide (Cr_2O_3) and silver. While higher pressures yielded high intensity peaks for elemental chromium and silver (m/z 52 and 107-109 respectively), lower pressures favor the formation of larger chromium clusters. These results are in agreement with previous work conducted by this group. While investigating the molecular energetics of GD-TOFMS using the thermometer molecule tungsten hexcarbonyl, Li et al found that

pressures between 0.2 to 0.6 torr were optimal for the “soft” ionization of large molecules. Higher pressures lead to extensive fragmentation, while extremely low pressures resulted in low analyte signal intensities.⁷

Operating Power: Although the operating power has little effect on the type of ionization garnered in the plasma, it greatly influences sputtering yields and ion intensities. Figure 3.8 shows the effects of operating power on the afterpeak mass spectra of a pellet mixed with 28% hexavalent chromium oxide (CrO_3) and silver. Under conditions of constant pressure and distance, increases in operating power yielded increases in ion intensities. This was especially noticeable for chromium oxide clusters, with only modest increases in the ion intensities of elemental chromium and silver.

Sampling Distance: While the optimal spatial distribution from which the GD is sampled is somewhat dependent on the analyte material under investigation, the metastable argon population tends to maximize approximately 5 – 10 mm from the cathode surface leading to enhanced molecular ion intensities in this region.^{7,18} Figure 3.9 shows the afterpeak mass spectra of a 20% hexavalent chromium oxide (CrO_3) and silver pellet taken at various distances from the sampling orifice. As the plasma is sampled farther out from the cathode surface, around 9mm, the ion intensities of chromium and chromium oxide clusters increase dramatically. Distances closer to the cathode (3 - 7 mm) show only lower mass chromium clusters, while farther distances (11 and 13 mm) have decreased intensities.

Figure 3.7. Effects of discharge pressure on the afterpeak mass spectra (5.1ms) of a pellet mixed with 30% chromium (III) oxide and silver. Operating power 120W and sampling distance 9 mm.

Figure 3.8. Effects of operating power on the afterpeak mass spectra (5.1ms) of a pellet mixed with 28% chromium (VI) oxide and silver. Discharge pressure 0.32 torr and sampling distance 9 mm.

Figure 3.9. Afterpeak mass spectra (5.1 ms) of a 20% chromium (VI) oxide and silver pellet taken at various distances from the sampling orifice. Discharge pressure 0.32 torr and operating power 120 W.

Table 3.2. Plasma Operating Parameters

Pellet Type		Pulse Time	Discharge Pressure	Operating Power	Sampling Distance
Chromium and Silver		5.1 ms	0.32 torr	120 W	9 mm
Chromium and Graphite		5.3 ms	0.32 torr	100 W	5 mm

3.3.3 Speciation and Quantitative Analysis

Differentiation of Pure Pellets: The mass spectra of hexavalent and trivalent chromium oxide in silver matrices are shown in Figures 3.10 and 3.11 respectively. Several Cr_xO_y^+ cluster ions and hydrogenated species were detected for both chromium oxides, although the number, relative intensity, and distribution vary depending on the particular chromium oxide. Specifically, chromium (VI) oxide produced more numerous and more oxygenated species with molecular ions containing up to four chromium atoms. These findings are in direct agreement with previous chromium speciation work conducted by Aubriet et al using secondary ion mass spectrometry (SIMS).^{9,14} The disparity in the number of cluster ions produced may be due to differences in ionization potential (IP), with the IP of hexavalent chromium closely matching that of metastable argon, 11.6 and 11.55 respectively. Specific ions were detected for both chromium oxides. Cr_2^+ and Cr_2O^+ (m/z 104 and 120) were characteristic of trivalent chromium oxide (Cr_2O_3), while CrO_3^+ (m/z 100) and numerous larger cluster ions, $\text{Cr}_{2-4}\text{O}_{4-12}^+$ (m/z 168, 184, 200, 252, 268, 284, 300, 352, 368, 384, and 400), were specific for the hexavalent chromium oxide (CrO_3).

Differentiation of Mixed Pellets: The differentiation between trivalent and hexavalent chromium oxide was also studied using a graphite matrix. Figure 3.12 shows the afterpeak mass spectra of a 20% chromium (III) oxide and graphite pellet and a 20% chromium (VI) oxide and graphite pellet. Although no specific peaks were detected for each oxidation state, the relative intensities of certain peaks allows one to easily discriminate between the two forms, in particular, the ratio of the CrO_3 - CrO_3H to Cr_2 cations (m/z 100 - 101 and 104 respectively). As would be expected, higher ion abundances of the Cr_2 ion is indicative of chromium (III) oxide (Cr_2O_3), while higher ion abundances of the CrO_3 ion is indicative of chromium (VI) oxide (CrO_3). Other specific markers include; m/z 120 – 121, corresponding to the Cr_2O and Cr_2OH cations, which are characteristic for the trivalent form, and appreciably higher intensities for m/z 68 – 69 and 84 – 85, corresponding to the CrO , CrOH , CrO_2 , and CrO_2H cations respectively, are characteristic of the hexavalent chromium oxide.

Mixed comparisons with varying ratios of the trivalent to hexavalent oxides in graphite were also performed. Figure 4.13 shows the afterpeak mass spectra of a pellet mixed with 15% chromium (III) oxide, 5% chromium (VI) oxide, and graphite and a pellet mixed with 5% chromium (III) oxide, 15% chromium (VI) oxide, and graphite. Using the same characteristic masses as stated earlier for graphite, one can quickly discern the oxidation state of greater quantity. Again, higher relative ion abundances for masses 104, 120, and 121 are indicative of Cr_2O_3 , while higher relative ion abundances for masses 100 or 101 are indicative of CrO_3 .

Quantitative Analysis: Differences in sample preparation, weighing, drying, mixing, and pressing, as well as plasma instabilities, can cause the relative intensities to deviate from a linear response. For this reason, an internal standard is often useful for quantitative analysis where the response from the instrument varies from run to run. Pellets were pressed using a 1% silver internal standard mixed with varying % concentrations of trivalent or hexavalent chromium oxide and spectroscopic grade graphite. The average intensities of the silver isotopes, m/z 107 and 109, were then used to normalize the relative intensities of several chromium and chromium oxide peaks: Cr, CrO_3 , Cr_2 , and Cr_2O (m/z 52, 100, 104, and 120 respectively). The average of at least five distinct measurements were calculated and plotted versus concentration. In Figure 3.14, the analytical calibration curves for chromium (III) oxide and chromium (VI) oxide in graphite are shown. The standard deviations between runs were calculated and are included by each point having error bars within the diameter of the marker on the plot. The R-square values for chromium (III) oxide and chromium (VI) oxide were found to be 0.9210 and 0.9222 respectively.

Figure 3.10. Afterpeak (5.1 ms) mass spectra of 20% chromium (VI) oxide with silver. Discharge pressure 0.32 torr, operating power 120 W, and sampling distance 9 mm.

Figure 3.11. Afterpeak (5.1 ms) mass spectra of 30% chromium (III) oxide with silver. Discharge pressure 0.32 torr, operating power 120 W, and sampling distance 9 mm.

Figure 3.12. Afterpeak (5.3 ms) mass spectra comparison of (A) a 20% chromium (III) oxide and graphite pellet and (B) a 20% chromium (VI) oxide and graphite pellet. Discharge pressure 0.32 torr, operating power 100 W, and sampling distance 5 mm.

Figure 3.13. Afterpeak (5.3 ms) mass spectra comparison of (A) a pellet mixed with 15% chromium (III) oxide, 5% chromium (VI) oxide, and graphite and (B) a pellet mixed with 5% chromium (III) oxide, 15% chromium (VI) oxide, and graphite. Discharge pressure 0.32 torr, operating power 100 W, and sampling distance 5 mm.

Figure 3.14. Calibration curves of (A) 5, 10, 15, and 20% chromium (III) oxide mixed with graphite and 1% silver, and (B) 5, 10, 15, and 20% chromium (VI) oxide mixed with graphite and 1% silver. Working conditions: 0.32 torr, 100 W, 5 mm, and 5.1 ms into the pulse cycle.

3.4 Conclusions

As with many transition metals, the toxicity of chromium is oxidation state dependent. Whereas the trivalent species of chromium (Cr(III)) is an essential nutrient needed in ultra-trace quantities, the hexavalent species (Cr(VI)) is toxic to humans and is a known carcinogen. It is for this reason that the ability to distinguish the valency of chromium is of great importance, a task defined under the broad definition of speciation. The data presented in this work demonstrate the suitability of Pulsed-GDMS for the direct speciation of chromium in solid state samples. Chromium (III) and chromium (VI) oxide samples were dried, mixed with matrices of spectroscopic grade silver or graphite by weight, and pressed into pellets. These pellets were then introduced into a pulsed rf glow discharge using a direct insertion probe and analyzed by time-of-flight mass spectrometry. Unique mass spectral features were found, permitting differentiation between the trivalent and hexavalent forms of chromium. Specifically signal at 104 and 120 m/z , corresponding to the Cr_2^+ and Cr_2O^+ cluster ions, is indicative of the presence of Cr(III) in the sample, while signal at 100 m/z , corresponding to the CrO_3^+ cluster ion, is indicative of the presence of Cr(VI). Discrimination was also achieved in mixed pellets with varying ratios of the trivalent to hexavalent oxides and calibration curves were constructed permitting quantitative analysis of each form in graphite. The R-square values from the calibration curves for chromium (III) oxide and chromium (VI) oxide were found to be 0.92 and 0.94 respectively.

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Chapter 4

Direct Manganese (Mn) Speciation in Solid State Materials by Pulsed Glow Discharge Time-of-Flight Mass Spectrometry

Abstract

Distinguishing and quantifying the specific oxidation states of elements in complex, solid state samples are very hard because extraction procedures often lead to changes in those oxidation states. Direct speciation in solid materials is highly desired because it precludes this extraction step and can enable retention of oxidation state information. In this work, pulsed glow discharge Time-of-Flight mass spectrometry is used to differentiate between manganese (IV) dioxide and manganese (II) monoxide directly in solid samples. The versatile pulsed glow discharge ion source can be tuned to establish the desired plasma environment for manganese speciation. The spatial and temporal characteristics of the glow discharge source are evaluated and optimized for such speciation by careful control of operating parameters, such as the supporting gas pressure and the operating power. Conditions are found that favor the production of the cluster ion Mn_2O_3^+ , characteristic for manganese (IV) dioxide. It is demonstrated here that once this has been accomplished, the two oxides can be differentiated and quantified.

4.1 Introduction

Chemical speciation, the process of identifying and quantifying the different species present in a material, continues to be of great interest to the analytical chemistry community. Speciation is generally considered to be subdivided into three categories: functional speciation, operational speciation, and specific oxidation state speciation.¹ Among these three, measuring the precise chemical form of an element is the hardest to achieve because it requires analytical methodology with the greatest selectivity and sensitivity.¹

The identification of the chemical state of transition metals is important because the nature of the chemical environment of such metals in compounds relates to their properties as a material or their origins in geology.² Traditional analysis focuses on the quantitative determination of the total concentration of the elements present in the material, but cannot help us understand the properties of the material containing the element. More importantly, the toxicity of a metallic compound is often a function of its chemical state.² As described in Chapter 3, chromium (III) is an essential trace element for the normal function of living organisms, whereas chromium (VI) is toxic and can cause allergic reactions and even cancer.³

Manganese is one of the most important transition metals and the 11th most abundant element in the Earth's crust.⁴ In nature, manganese occurs in the Mn (II), Mn (III) and Mn (IV) oxidation states. These valences appear in a wide range of oxide

minerals, including manganosite (MnO) and pyrolusite (MnO_2).⁵ In the environment, manganese broadly disperses throughout soils, sediments, water and biological materials. In marine sediments, chemical speciation is very important because particulate manganese oxides play a significant role in benthic biogeochemical processes.³ The widespread use of manganese in industry has led to its presence in the surrounding environment⁶ at concentrations and in forms significantly different from the natural background. Manganese is generally considered an element of very low toxicity except in humans where it acts on the central nervous system.⁷ Chronic overdose or moderate exposure over an extended time period may result in severe neurological disorders characterized by the disruption of movements.⁷ The chemical form in which manganese exists determines its bioavailability and can cause either positive or negative effects on the environment as well as impact its toxicity.⁸ It was found that Mn (II) provides significantly more bioavailability for Mn than Mn (IV).⁹

For all chemical speciation, it is essential not to disturb the system during sampling, pretreatment and measurement, lest a change be induced. To distinguish and quantify the specific oxidation states of elements for solid samples is very hard to achieve because extraction procedures tend to change the speciation.¹ Analytical techniques for the study of transition metal speciation can be divided into two classes: indirect methods and direct methods.¹⁰ Indirect methods require the sample to be in a liquid phase for analysis and are often termed “wet chemistry” approaches for this reason. The most commonly used indirect methods include UV/visible spectroscopy, atomic absorption spectroscopy, and electrochemical techniques.⁴ Unfortunately, these methods have their

limitations. First, the classic wet chemistry technique requires that the sample be dissolved to yield a solution sample, which makes the sample preparation step more complex and time consuming. Second, wet chemistry requires the use of expensive and sometimes toxic solvents, which increase the analysis cost. Third, these additional pretreatment procedures, for example extraction, preconcentration or derivatization can induce oxidation or reduction reactions thereby altering the chemical state of a metal in the original sample.² Direct methods are capable of studying solid state samples in their native form without need for sample dissolution. These methods are becoming more and more important for environmental and health applications and for use in materials science.¹¹ For many environmental, geochemical and materials science determinations, it is necessary to preserve the sample in its natural condition and to avoid modifications during analysis.¹² The most widely used techniques for direct elemental speciation analysis in solid samples are X-ray absorption spectroscopy and Raman spectroscopy.⁴ Compared to indirect methods, analyzing a solid sample directly affords the following advantages: less analysis time, lower cost, less risk of contamination, and less destruction of the sample. When considering the current direct, non-destructive methods, they may be able to identify the species but unable to quantify it without associated separation procedures because they are not sufficiently sensitive.¹

In elemental speciation, two different levels of information are sought. The first of these is the determination of relative elemental abundances. The second level is the determination of the oxidation state by identifying information regarding the chemical environment of the element. The ideal speciation technique should provide elemental,

structural and molecular information in order to provide these determinations. To accomplish this, the technique needs to be able to determine the specific composing elements and structural fragments and also be able to set free the individual molecules from the solid material by breaking the intermolecular bonds without affecting the intramolecular ones.¹² Interestingly our group has found the glow discharge coupled with mass spectrometry to provide a new technique for direct speciation of solid state samples.

Mass spectrometry in combination with a direct soft ionization technique for solids is known as a potential solution for this problem.¹³ For example, laser ablation mass spectrometry (LA-MS), laser microprobe mass spectrometry (LMMS) and static secondary ion mass spectrometry (s-SIMS) are the most employed mass spectrometry techniques in this area.¹³ It is reported that speciation of the first row transition metal oxides can be done and the chemical state of some transition metals can be identified between different oxidation states by these methods.²⁻⁴ Under selected experimental conditions, characteristic cluster ions can be produced that correspond to different oxidation states of the transition metal. By use of these characteristic ions, ion abundance ratios, and application of plog's methods the specific chemical state is differentiated.² Glow discharge mass spectrometry (GD-MS) would fall into this category of approaches.

The glow discharge is a low energy ion source that has been extensively used for the direct trace elemental analysis of solid samples over the past 30 years.¹⁴ Different from the inductively coupled plasma, the glow discharge relies on sputtering processes for sample atomization followed by and plasma collisions leading to excitation and ionization.¹⁵ Its application was expanded to application with nonconductive materials by the introduction of radio frequency glow discharge devices.¹⁶ Pulsing the glow discharge power can increase the ionization efficiency achieved without overheating the sample.²² Another big advantage brought about by pulsed operation is the temporal resolution of analytical species, which makes it possible to promote analyte signal while discriminating against signal from potentially interfering discharge gases.^{17,18} Recent developments in pulsed glow discharges have focused on their tunability and capability in molecular speciation analysis. This work takes advantage of the various excitation and ionization pathways and their presence or absence during different phases during the lifetime of a discharge pulse. Through the selection of appropriate conditions, for example, the discharge gas, pressure, power or time regime, the plasma can be tuned and thus provide a specific ionization environment for the type of chemical information desired.¹⁹

Recent reports have shown that glow discharge mass spectrometry is a very promising technique for chemical speciation. For example, Lewis et al. reported that elemental, structural and molecular weight information of each species can be obtained at the same time through time gated detection of a pulsed GD time-of-flight mass spectrometer coupled with gas chromatography.²⁰ In Li et al.'s work, the internal energy

distributions of a millisecond pulsed rf glow discharge plasma were studied by using tungsten hexcarbonyl as a thermometer molecule.²⁷ Temporal and spatial variations in the glow discharge ionization were investigated as well. A key application found in that work was the direct determination of bromine concentrations in flame-retardant plastics.²¹

In this study, millisecond-pulsed glow discharge time-of-flight mass spectrometry is used to differentiate between the chemical forms of manganese, Mn (II) and Mn (VI), directly in solid state samples. Temporal and spatial characteristics of the pulsed GD were evaluated and are discussed. The effect of glow discharge operating conditions, discharge gas pressure and operating power, on ion signals was also investigated. Quantitative analysis was performed under these optimized conditions. This builds upon previous work in which the method was applied to the speciation of Cr (VI) and Cr (III). The current study that emphasizes the systematic optimization of glow discharge conditions and quantitative analysis of manganese, another element with both positive and negative effects on living systems depending on its chemical form.

4.2 Experimental

4.2.1 Pulsed Glow Discharge Plasma Device

The power supply system used for the glow discharge plasma is a 13.56 MHz radio frequency (rf) generator equipped with an automatic matching network (RF Plasma

Product Inc., Marlton, NJ). The internal power control pulsing mode of the rf power supply permits control of applied power, pulse width, and duty cycle. The rf pulse width was set at 5 ms with 25% duty cycle while the operating power was set at 80 W. Argon (ultra pure, Airgas, Randor, PA) as the discharge support gas was introduced into the glow discharge chamber through a metering valve to control the gas pressure. A thermocouple pressure gauge (Varian, Lexington, MA) was used to monitor the discharge pressure in the chamber.

4.2.2 Time-of-Flight Mass Spectrometer

Mass spectrometric measurements were made using a linear time-of-flight instrument (R.M. Jordan Co., Grass Valley CA) oriented orthogonally to the ion beam from the glow discharge. Detailed information about the TOF mass spectrometer and data acquisition system has been described previously.²² A six-way, high vacuum cross (MDC Vacuum Products Co., Hayward, CA) attached to the TOF flange served as the glow discharge chamber. The probe inlet consisted of a ball valve that allows direct probe insertion without breaking the vacuum. Disk samples with a 5 mm diameter and 3 mm thickness loaded on the tip of the direct insertion probe were used as cathodes to produce the plasma. The samples were shielded by a nonconducting MACOR® shield (Accuratus, Washington, N.J.) to confine sputtering to the sample top surface. The TOF sampling distance can be adjusted by changing the direct insertion probe (DIP) position along the axial direction. Ions were sampled from the GD chamber by an exit orifice and introduced into the mass analyzer's flight tube by pulsing the TOF repeller. The

application of a 1 μ s ion extraction pulse is triggered by a digital delay generator (EG&G Princeton Applied Research, Princeton, NJ) which is synchronized with the rf power pulse to initiate the signal detection system. The ions produced from a specific time region within the power pulse sequence can be monitored by the delay time set from the digital delay generator (Figure 4.1). The mass spectrometric signal was amplified and fed into a 1-GHz oscilloscope (LeCroy 9370M, Chestnut Ridge, NY). After being digitized and averaged continuously at 1:1023, the spectral data were transferred to the computer and imported into a Microsoft Excel spreadsheet program through a GPIB card for construction of the corresponding mass spectrum. All operating conditions were optimized to yield maximum signal for the manganese oxides species. Table 4.1 shows the typical pulsed rf glow discharge time-of-flight mass spectrometer operating parameters.

Figure 4.1 The schematics of the TOF mass spectrometer and the diagram of time-gated data acquisition system

Glow discharge

Pressure	0.2-0.8 Torr
Operating power	80-100 W
Pulse duration	5 ms
Duty cycle	25%
Sampling distance	2-25 mm

Time-of-Flight

Flight path length	1 m
Ion lenses potential	
Skimmer	-230 V
Extractor	0 V
Accelerator/flight tube/X2/Y2	-1531 V
Deflector (X1)	-1786 V
Deflector (Y1)	-1550 V
Repeller	+250 V
Detector	-1880 V

Vacuum Conditions

Intermediate stage	10^{-5} Torr
Flight tube	10^{-6} Torr

Table 4.1 Pulsed millisecond rf GD TOF-MS operation parameters

4.2.3 Sample Preparation and Sample Introduction

Analytical reagent grades of manganese (II) monoxide (MnO) and manganese (IV) dioxide (MnO₂) were purchased from commercial suppliers (Alfa Aesar, Ward Hill, MA). The manganese oxides were mixed with spectroscopic grade silver powder (Alfa Aesar, Ward Hill, MA) at different concentrations (20%, 25%, 30%, 35%, and 40%) by weighing. Spectroscopic grade copper powder (Matheson Company Inc., East Rutherford, N.J.) at 10% w/w was added to the mixture as an internal standard for quantitative experiments. The mixed powders were homogenized for 3 min using a laboratory mixer (Wig-L-Bug, SPEX, Edison, NJ). Each mixture was compacted under 5000 psi for 2 min. The resulting sample disk was 5 mm in diameter and 3 mm in height.

After inserting the compacted sample into a machined stainless steel sample holder, the entire assembly was mounted onto the DIP via a push-on connector (see Figure 4.2). An aluminum sleeve covering a MACOR® jacket was used to shield the sample and sample holder leaving only the top surface of the manganese sample exposed to the plasma. The DIP was inserted into the glow discharge chamber and the plasma was initiated after 15 min under vacuum.

Compacted Sample Assembly

Figure 4.2 (a) The schematics of the glow discharge chamber and sample introduction system (b) the schematic presentation of the compacted sample assembly

4.3 Results and discussion

4.3.1 Evaluation of Temporal Regimes

Temporal regimes were studied by comparing a pure silver matrix sample with a mixed sample containing 25% MnO_2 or MnO and 75% silver by weight. Experimental conditions for both samples were consistent: 0.4 Torr Ar discharge gas, 80 W rf glow discharge power, 10 mm distance between the sample cathode sampling orifice. Figure 4.3-4.5 shows the mass spectra of pure silver, 25% MnO_2 mixed with silver and 25% MnO mixed with silver at different time regimes.

0.2 ms 25%MnO₂+Ag

0.3 ms (a) Pure silver

(b) 25%MnO₂+Ag

(c) 25%MnO+Ag

Figure 4.3 Time resolved mass spectra of (a) Pure silver (b) 25%MnO₂+Ag (c) 25%MnO+Ag during the prepeak (0.2 ms and 0.3 ms). Discharge pressure 0.4 Torr, operating power 80 W, and sampling distance 10 mm.

(a) Pure silver

(b) 25%MnO₂+Ag

(c) 25%MnO+Ag

Figure 4.4 Time resolved mass spectra of (a) Pure silver (b) 25%MnO₂+Ag (c) 25%MnO+Ag during plateau (4.9 ms). Discharge pressure 0.4 Torr, operating power 80 W, and sampling distance 10 mm.

(a) Pure silver

(b) 25%MnO₂+Ag

(c) 25%MnO+Ag

Figure 4.5 Time resolved mass spectra of (a) Pure silver (b) 25%MnO₂+Ag (c) 25%MnO+Ag during afterpeak (5.3ms) Discharge pressure 0.4 Torr, operating power 80 W, and sampling distance 10 mm.

Prepeak: The main ionization mechanism during the prepeak is electron ionization, because of the presence of the high flux electron beam. Spectra collected at 0.2 ms and 0.3 ms show typical prepeak mass spectra. At 0.2 ms the discharge gas has just broken down to form Ar^+ ions at 40 m/z and ArH^+ at 41 m/z. Also some of the residual gas such as air and water is broken down by the high voltage applied between the sample cathode and anode and causes the smaller peaks around 20 m/z. From the spectra, there are no species from cathode observed because of the delay between sputtering and diffusion. In the glow discharge, the discharge gas ions must form first, and then these ions sputter the sample cathode and release the neutrals which will be ionized later. At 0.3 ms, the population of Ar^+ ions continues to increase with the application of the high voltage. These Ar^+ ions collide with each other to produce argon dimers Ar-Ar^+ at 80 m/z. Attracted by the negative potential, argon ions accelerate and collide with the sample cathode sputtering analyte species into the gas phase, thus silver appears in the spectrum at 107 and 109 m/z. As more argon gas ions form and sputter the manganese oxide and silver surface, the more sputtered manganese atoms and oxides are released into the GD plasma where they are subsequently ionized. The population of these ions increases over the time frame of about 1 ms until reaching a steady-state value. There is no significant difference between pure silver and 25% MnO_2 or 25% MnO mixed with silver because the manganese oxide species are not detected at this time.

Plateau: Spectra from the plateau regime were collected by setting the repeller pulse 1.0-5.0 ms from the start of the pulse cycle. From 1.0 ms until the termination of power, the glow discharge is in a steady state. This portion of the pulsed glow discharge is

similar to that of the continuous glow discharge. The plateau regime is most useful for determining analyte structure, because extensive fragmentation is obtained through the combination of electron impact, charge transfer, and Penning ionization. At this time, signal from both the discharge gas and the cathode material are obtained. Mass spectra obtained at 4.9 ms for each of the three samples are shown in Figure 4.4. When compared to the prepeak regime, spectra taken during the plateau exhibit silver peaks with much higher intensities. In the spectrum of manganese oxide mixed with silver, stable signals for manganese at m/z 55 and for the silver isotopes at m/z 107 and 109 are obtained. Populations of both sputtered species (silver and manganese) and non-sputtered species (argon) have reached a steady-state value. There is still no difference found between spectra of MnO_2/Ag and MnO/Ag .

Afterpeak: After power termination, the population of neutral species remains relatively stable whereas the electrons are cooled down rapidly because of the disappearance of the electric field. These electrons can recombine with argon ions to produce a large amount of argon metastable atoms. Thus, with the increase in metastable atoms and the disappearance of both ionizing electrons and argon ions, Penning ionization is the main mechanism to ionize the manganese samples during the afterpeak. One characteristic of Penning ionization is its selectivity, which means it only ionizes species with ionization energy at or below 11.72 eV for metastable argon atoms. Many common contaminants exist in the glow discharge that cannot be ionized by metastable argon atoms, while the sputtered species are efficiently Penning ionized. This makes the afterpeak mass spectra rich in analyte signal but minimal in background contaminant

signal. With a time delay of 5.3 ms, the ion signal intensities for the cathode material maximize and become the dominant feature of the mass spectrum. The ion intensity of Ag is increased drastically and the Ag-H₂O complex (m/z 125 and 127) and Ag dimer (m/z 214 and 218) can also be seen. Comparing spectra for MnO₂/Ag and MnO/Ag, the cluster ion Mn₂O₃⁺ (formed at 158 m/z) was detected for the MnO₂/Ag sample, while no specific cluster ion was found for the MnO/Ag sample.

This work focuses on the direct chemical speciation between MnO₂ and MnO from solid state materials. Whereas there is no difference between MnO₂ and MnO in the prepeak and plateau mass spectra, specific cluster ions appear in the afterpeak regime mass spectra for MnO₂. Thus, in all further spectra the afterpeak region was chosen for the differentiation of MnO₂ and MnO.

Figure 4.6 Delay time setting selection study on (a) Mn^+ (b) MnO^+ & Mn_2O_3^+ during afterpeak. Discharge pressure 0.4 Torr, operating power 80 W, and sampling distance 9 mm.

To select the best delay time during the afterpeak time regime, the effect of this setting on several species of interest was studied by varying the delay time via a digital delay generator. The species monitored were Mn^+ , MnO^+ , and Mn_2O_3^+ . Other glow discharge operating conditions were kept constant: 0.4 Torr argon discharge pressure, 80 W operating power, and 9 mm sampling distance. Plots of signal intensity as a function of the delay time set within the afterpeak region are shown in Figure 4.6. The ion intensity for both manganese oxide and manganese clusters increased with the delay time increasing from 5.0 ms to 5.3 ms. At 5.3 ms these intensities reach a maximum and then decrease with further increases in the delay time. During the afterpeak regime, Penning ionization is the main ionization process because of the large amount of metastable argon atoms. At around 5.3 ms, the population of metastable argon atoms has reached its highest concentration while the concentration of the neutral manganese species remains relatively unchanged. The signal begins to wane around 5.5 ms with the depletion of these argon metastable atoms. Based on these results, the speciation and quantitative analysis of the manganese oxide samples were performed at 5.3 ms.

4.3.2 Evaluation of spatial variations

It is important to study the spatial dependence of the ion population, which helps to determine the optimum sampling distance to maximize analytical sensitivity. In the glow discharge, each species has a characteristic spatial distribution and so does their excitation and ionization processes.²⁵

The effect of sampling distance on manganese species was studied for 25% manganese dioxide with silver at 5.3 ms under conditions of 0.4 Torr discharge pressure and 80 W operating power. The sampling distance is the measured distance between the cathode and the sampling orifice. By changing the probe position, the sampling distance was adjusted between 3 to 20 mm. At distances smaller than 3 mm the cathode is too close to the sampling plate and the plasma is extinguished, while at distances farther than 20 mm the cathode is too far away and the signal is too weak to study.

(a)

(b)

Figure 4.7. Spatial evaluation of 25%MnO₂+ Ag during afterpeak (5.3 ms). Sampling distance effect on (a) Mn⁺ (b) MnO⁺ & Mn₂O₃⁺. Glow discharge pressure 0.4 Torr, operating power 80 W

In Figure 4.7, the ion signal intensities of Mn^+ , MnO^+ and Mn_2O_3^+ were plotted against sampling distance. In Figure 4.7(a), the signal intensity of Mn^+ ions increased from 3 to 10 mm, reached a maximum plateau value from 10 to 13 mm, and then decreased at distances further than 13 mm. In Figure 4.7(b), the intensity of MnO^+ ions quickly increased from 3 mm and maximized at 5 mm, then slowly decreased back to baseline at 20 mm. For the Mn_2O_3^+ cluster ions, their plot looks similar to the one for MnO^+ , but the peak shifted to a larger distance 7 mm. This is because the Mn_2O_3^+ cluster ions are formed from the MnO^+ ions. When the MnO^+ ions reach their highest concentration, the plasma environment will favor cluster ion formation. The cluster ions intensity kept increasing from 3 to 7 mm and then slowly decreased back to baseline. The optimized distance for cluster ion formation is from 6 to 9 mm. A previous study in this lab found that the metastable argon atom density maximized at around 8 mm during the afterpeak regime using atomic absorption measurements.²³ Also, Penning ionization was maximized at this distance too.²⁴ The agreement between these results indicates that the ionization of the cluster ions is mainly caused by Penning ionization during the afterpeak regime.

4.3.3 Evaluation of glow discharge operating parameters

Glow discharge operating parameters can affect the excitation and ionization processes significantly. By tuning the operating parameters, a specific chemical physical plasma environment can be produced to favor the formation of the species of interest.

Pressure effects

Among these parameters, the discharge gas pressure is considered to be one of the most important, requiring careful study and control. Different discharge gas pressures can result in a significant change in the mass spectra obtained because pressure affects both the mean free path and the collision frequency. When the pressure is lower than 0.2 Torr, the glow discharge is not stable and there is no mass spectrum formed. When the pressure is too high, the cluster ions are dissociated by the high collision frequency and their ion intensity decreases. According to Lei Li's work,²⁵ the optimal discharge pressure lies between 0.2 to 0.6 Torr for argon gas. An investigation of the pressure effect was conducted for discharge pressures ranging from 0.2 to 0.6 Torr. In these studies, the operating power was fixed at 80 W and the sampling distance was fixed at 10 mm. In Figure 8, ion signal intensities of manganese species are plotted against the discharge gas pressure for the afterpeak regime at 5.3 ms. The sample used in these experiments is a pellet formed from 25% Manganese dioxide mixed with 75% silver. From Figure 8(a), when the pressure increases from 0.2 to 0.6 Torr, the Mn^+ ions increase as well. The concentration of Mn_2O_3^+ cluster ions reaches a maximum near 0.35 Torr. When the discharge pressure increases, the number of Ar atoms increases, and so does the number of argon metastable atoms. In the afterpeak regime, which in this experiment was set at 5.3 ms, more Mn atoms will be Penning ionized by the increase in collisions with argon metastable atoms. From Figure 8(b), the MnO^+ ions increase in intensity with an increase in pressure from 0.2 to 0.3 Torr, then decrease from 0.3 to 0.6 Torr. More MnO species are ionized by argon metastable atoms at pressures between 0.2 and 0.3 Torr. When the

pressure continues to increase, the formed MnO^+ ions decrease because of enhanced CID. A similar situation exists for Mn_2O_3^+ cluster ions; lower or higher pressures do not favor the cluster ion formation. The optimal discharge pressures are between 0.3 and 0.4 Torr for cluster ions.

(a)

(b)

Figure 4. 8 Pressure study of 25%MnO₂+Ag during afterpeak (5.3 ms) on (a) Mn⁺ (b) MnO⁺ & Mn₂O₃⁺ Operating power 80 W, sampling distance 10 mm

Power effect

The influence of power on the manganese species signal intensities was examined by varying the operating power from 20 to 120 W. A pellet of 25%MnO₂ in Ag was used as the sample. The discharge gas pressure remained at 0.4 Torr and the sampling distance was fixed at 9 mm. Previous work in this lab observed that the operating power has a significant effect on ion signal intensities but has a negligible influence on energy distributions. In Figure 4.9, ion intensities of the manganese species are plotted against the operating power. When the power is increased, the Mn⁺ and MnO⁺ ions increase in intensity from 20 to 100 W and the Mn₂O₃⁺ ions increase in intensity from 20 to 80 W. This is because both sputter rate and ionization efficiency are enhanced by an increase in operating power. Notice there is a decrease in signal intensity for Mn⁺, MnO⁺, and Mn₂O₃⁺ at powers beyond 100 W. At high operating powers, in this case higher than 100 W, the plasma will become unstable leading to reductions in signal stability.

(a)

(b)

Figure 4. 9 Power effect of 25%MnO₂+Ag on (a) Mn⁺ (b) MnO⁺ & Mn₂O₃⁺. Glow discharge pressure 0.4 Torr, sampling distance 9 mm, afterpeak time regime 5.3 ms

Quantitative Study:

Manganese (IV) dioxide and manganese (II) monoxide can be differentiated under the optimized conditions employing the specific cluster ion Mn_2O_3^+ at 158 m/z characteristic for manganese dioxide. Both MnO_2 and MnO produce MnO^+ ions. The quantitative analysis of manganese oxides was performed by mixing silver powder and 10% copper powder with different concentrations (20%, 25%, 30%, 35%, 40%) of manganese oxides under the optimized conditions of 0.4 Torr discharge gas pressure, 9 mm sampling distance, 80 watts operating power, and a delay gate of 5.3 ms.

Silver is chosen as the host matrix because it can increase the electrical conductivity of the compacted sample. The sputter atomization and ionization are both enhanced by increasing the sample conductivity. Thus more intense analyte signals can be observed. Copper powder was added into the mixture at 10% as an internal standard to account for variations in sample preparation and plasma instability. The intensity of the copper isotope peak at 65 m/z was used to normalize the relative intensities of manganese, manganese oxide and manganese oxide cluster peaks at 55 m/z, 72 m/z and 158 m/z respectively.

Calibration curves for both MnO_2 and MnO were constructed with the data collected from the 5 manganese oxide standards mixed with copper and silver. For each concentration, at least three replicate measurements were averaged and the standard deviations were calculated. The mean normalized intensity was plotted versus the

concentration of manganese oxide in the sample with the relative standard deviation marked as an error bar. The calibration curves represent the linear regression of the data collected. The regression data was calculated using an Excel spreadsheet and the correlation coefficients for the calibration curves are shown below the equation by the R-squared value.

Figure 4.10 MnO^+ Calibration Curve for MnO_2 standards ($\text{MnO}_2/\text{Ag}/10\%\text{Cu}$)

LOD 4.30%

Figure 4.11 Mn_2O_3^+ Calibration Curve for MnO_2 standards ($\text{MnO}_2/\text{Ag}/10\%\text{Cu}$)

LOD 9.07%

Figures 4.10 and 4.11 are calibration curves using normalized intensities for the cluster ions MnO^+ and Mn_2O_3^+ respectively from a series of manganese dioxide standards. Figure 4.10(a) is a calibration curve with standard concentration ranges from 20% to 40% MnO_2 . The linearity of this calibration curve is quite good ($m = 7.8$ mV/ $\text{MnO}_2\%$, $b = -83.3$ mV, $R^2 = 0.9688$). In Figure 4.10(b), a blank sample, made from 90% Ag with 10% Cu, is added into the calibration curve to calculate the limit of detection. The resultant calibration curve still exhibits good linearity ($m = 5.8$ mV/ $\text{MnO}_2\%$, $b = -21.4$ mV, $R^2 = 0.9509$). The 3σ detection limit for MnO_2 calculated from the background noise²⁶ is 4.30% when using MnO^+ .

In Figure 4.11, Mn_2O_3^+ cluster ions were used to plot the calibration curve. The linearity of the calibration curve is also quite good ($m = 2$ mV/ $\text{MnO}_2\%$, $b = -15.7$ mV, $R^2 = 0.9668$). After the addition of a blank to the calibration curve, the linearity improved ($m = 1.8$ mV/ $\text{MnO}_2\%$, $b = -10.5$ mV, $R^2 = 0.9873$). The detection limit for MnO_2 was calculated to be 9.07% using the Mn_2O_3^+ cluster ion, which is higher than when MnO^+ was used.

In Figure 4.12, a calibration curve for MnO^+ was constructed with the data collected from a series of manganese (II) monoxide standards mixed with copper and silver. The calibration curve shows excellent linearity ($m = 3$ mV/ $\text{MnO}_2\%$, $b = -4.2$ mV, $R^2 = 0.9861$). Improvements to the linearity ($m = 3.1$ mV/ $\text{MnO}_2\%$, $b = -5.1$ mV, $R^2 = 0.9965$) were obtained when a blank MnO sample was added to the calibration curve. The detection limit was calculated to be 2.81% for manganese monoxide.

Figure 4.12 MnO^+ Calibration Curve for MnO standards (MnO/Ag/10%Cu)

LOD for MnO 2.81%

4.4 Conclusion

Chemical speciation between manganese (IV) dioxide and manganese (II) monoxide was obtained directly from solid-state samples using rf pulsed-GDMS. The specific cluster ion, Mn_2O_3^+ , detected only in the manganese (IV) dioxide sample was used to differentiate between these two manganese oxides.

The temporal and spatial variations were evaluated as well as the influence of glow discharge operating parameters (pressure and power) on signal intensity. The afterpeak regime was chosen for speciation measurements because its softer ionization mechanism favors the production of cluster ions used to differentiate between the two manganese oxides. The experiment shows that at 5.3 ms, during the afterpeak regime, the ion intensities of all the manganese species of interest were maximized, thus it was selected as the gated delay time to collect mass spectra. The optimal discharge pressures were found to be 0.3-0.4 Torr. At lower pressures, the plasma is unstable, while at higher pressures the increased CID leads to extensive fragmentation and hinders the formation of the cluster ions.

The operating power was found to affect the signal intensity significantly. The higher the operating power used, the more intense the signal became. But the plasma became unstable when the power was too high. The best operating power was found to be 80 W and the optimal sampling distance was found at around 8 mm from the cathode surface.

This research demonstrates that the pulsed glow discharge ion source exhibits utility for manganese speciation when controlled temporally and spatially. By carefully tuning all the related parameters, a specific desired plasma environment can be produced to support the formation of the cluster ions used for speciation.

Through the combination of these optimized parameters, the signal intensities were increased and the quantitative analysis of the two manganese oxides was demonstrated. The calibration curves were constructed using the cluster ions Mn_2O_3^+ and MnO^+ . All curves showed excellent linearity and good precision for both manganese oxide quantitative analyses. The fast sample preparation and data collection makes this method a quick and easy one compared to traditional chemical speciation methods, though the limit of detection is poor. Future work will focus on the speciation of manganese oxide mixtures and the theoretical study of cluster formation within the plasma.

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