EVALUATION OF NOVEL PROJECTILES AND THEIR IMPACT ON SECONDARY ION MASS SPECTROMETRY

An Undergraduate Research Scholars Thesis

by

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ABSTRACT

Evaluation of Novel Projectiles and Their Impact on Secondary Ion Mass Spectrometry

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A distinct feature of secondary ion mass spectrometry, SMIS, with large projectiles, e.g. C_{60}, Au_{400}, Ar_{2000}, is abundant secondary ion, SI, emission. Thus it is feasible to run experiments in the event-by-event bombardment detection regime, where SI's from each individual projectile impact are recorded separately. A sequence of impacts amounts to probing a set of nanospots, as the ejecta originate each time from an area of 10-15 nm in diameter. To date we have developed nano analysis with Au_{400}^{4+} viz. n/q=100, produced with a liquid metal ion source, LMIS. The purpose of this study, was to pursue this approach with still more massive projectiles. We found that the LMIS can produce projectiles measured to have n/q values of 200 to 350. A first task was to characterize the novel projectile by identifying the number of constituent atoms and the charge of each projectile. This was accomplished by implanting the projectile into highly oriented pyrolytic graphite (HOPG) and performing Neutron Activation Analysis (NAA). By NAA, it was determined that the number of constituent atoms corresponding to n/q=100 and n/q=350 where 400 and 2800 respectively. A second objective was to determine if the more massive projectiles can produce more analyte specific secondary ions without increasing fragmentation. A library of mass spectra corresponding to different size gold clusters (n/q=100,200,350), was created for various samples (glycine, cysteine, Gramicidin S, etc.).

When bombarding each sample with n/q=100 and n/q=350, the number of analyte specific secondary ions roughly doubled showing a promising future for these massive projectiles. For glycine we measured an increase from 1 to 2.6 molecular ions per impact when increasing the size of the projectile from n/q=100 to n/q=350. These massive projectiles show a promising enhancement in the performance of SIMS.

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NOMENCLATURE

HOPG	Highly Oriented Pyrolytic Graphite
LMIS	Liquid Metal Ions Source
NAA	Neutron Activation Analysis
n/q	Number of Constituent Atoms over Charge
SIMS	Secondary Ion Mass Spectrometry
PC	Personal Computer
TDC	Time to Digital Converter
ToF	Time of Flight

CHAPTER I

INTRODUCTION

In the past decade Secondary Ion Mass Spectrometry (SIMS) has been very influential in many fields of research from biomedical to microelectronic, but recently it has reached a new acme.[1] In past studies, individual or small clusters of gold e.g. Au^{+}, Au^{3+}, Au^{9+} have been used to bombard a surface of interest for molecular characterization. Recently, there has been a growing interest in larger gold clusters for nanoscale analysis. This is due to the fact that massive gold clusters promote the emission of molecular ions.[2]

The purpose of this study is to explore analysis with even still more massive projectiles. This involves their characterization, determination of number of atoms in a single cluster, their charge state, and the size of the cluster. The experiments presented here provide an approach to obtain larger mass clusters as well as an examination of these novel projectiles and the effect they could have on the secondary ion emission of two organic samples.

In order to properly characterize the novel projectiles used in these experiments, the number of constituent atoms and the charge of each projectile was identified. This was accomplished by implanting the projectile into highly oriented pyrolytic graphite (HOPG) and performing Neutron Activation Analysis (NAA). Neutron Activation Analysis (NAA) is a useful technique in the precise determinations of elemental compositions. This technique is derived from the fact that most elements, when bombarded with neutrons, will form a radioactive isotope that will emit gamma rays that are characteristic of the nucleus that emits them. By measuring the number of gamma rays emitted, we can calculate the number of atoms implanted into the

HOPG. With this information, and the n/q value measured from the implantation of our projectile into the HOPG, it is possible to determine the charge of each individual cluster.

In our experiment, Glycine, the simplest of the 20 amino acids found in proteins[3], and Gramicidin S, a common antibiotic used for medical applications[4] , were bombarded with massive projectiles secondary ions are mass analyzed using a reflectron ToF mass spectrometer. The sample was probed by single stochastic bombardments on the target with each massive projectile having an emission volume of 10-20 nm in diameter and 5-10 nm in depth allowing for nanoscale analysis. [5]

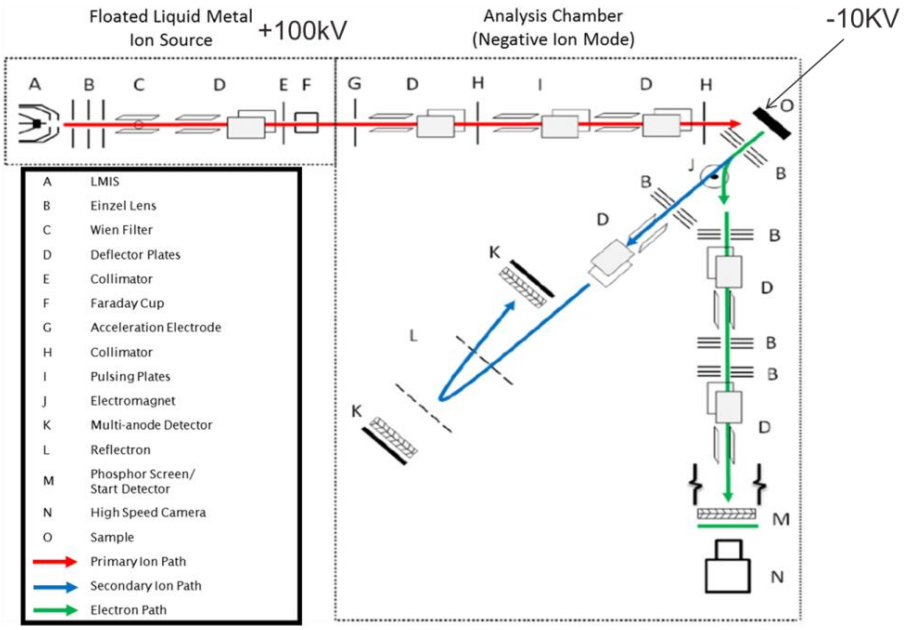
CHAPTER II

METHODS

Instrumentation

Time of Flight Mass Spectrometer

This experiment uses a liquid metal ion source (LMIS) filled with a gold-silicon eutectic (3wt% silicon) this allows for the production of a wide range of gold projectiles i.e. Si^{+}, Au_1^{+}, Au_9^{+}, Au_{2100}^{6+}. Specifications of the LMIS can be found in [6]. The primary ion column consists of a LMIS, focusing lens, and a Wien filter shown in Figure 1.



Eller, Michael J., Stanislav V. Verkhoturov, and Emile A. Schweikert. "Testing Molecular Homogeneity at the Nanoscale with Massive Cluster Secondary Ion Mass Spectrometry." *Analytical Chemistry Anal. Chem.* (2016): n. pag. Web.

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Figure 1. Schematic of instrumentation used for SIMS analysis in event-by-event bombardment/ detection mode.

The experiments where conducted using a custom built SIMS equipped with a reflection time of flight, ToF, mass spectrometer. A schematic of this instrumentation can be found in Figure 1. In summary, a primary ion beam is produced by extracting gold from the LMIS (imbedded in a 100kV platform). The beam is focused by a lens into the Wien filter which selects the desired projectile using a magnetic field crossed to an electric field. After the Wien filter, the selected projectile beam is accelerate with 100keV towards a pulser. The beam is then pulsed to a rate of 1,000 projectiles/sec and then collimated to insure each projectile is separated in time and space. A single projectile strikes the sample, which is biased to -10kV upon impact. Electrons, neutrals, and secondary ions are emitted from the sample. Electrons are deviated using a weak magnet and act as the start of the ToF. Concurrently, secondary ions are mass analyzed. The secondary ions are detected using two 40mm micro channel plate chevron multipliers and an 8 anode stop detector. The multi-anode detector enables the detection of up to 8 isobaric ejecta. The ToF mass spectrum is collected by a time to digital converter, TDC, and stored on a PC. [6]

Nuclear Reactor

The technique used was instrumental neutron activation analysis (INAA). The comparator method of INAA—in which calibrators and the unknown samples are irradiated and gamma-ray counted under identical conditions—was employed. The neutron irradiations were performed in the A4/A6 irradiation position of the TEES Nuclear Science Center 1 MW TRIGA reactor. The subsequent gamma-ray spectrometry was performed using a high-purity Ge (HPGe) gamma-ray detector (from Canberra Industries), and the data reduction was done using NAA software from Canberra Industries.

Sample Preparation

Silicon wafers (Silicon Valley Microelectronics, Santa Clara, CA) where cut into 1cm X 1cm squares and sonicated in absolute ethanol. Two samples were prepared in this experiment. 5 mg of Glycine (purchased from Sigma Aldrich) was vapor deposited on a silicon wafer. The second sample was generated by drop casting ~10µl of 10mg/ml gramicidin s (purchased from Sigma Aldrich) in methanol onto a silicon wafer.

Software

The mass spectrums were analyzed using SAMPI software solution (version 4.3.26), an in-housed custom written software developed with LabWindows/CVI 2010 version 10.0.0 (National Instrumentation Corporation, Austin TX).

The graphs presented in this paper were constructed using Origin software (version 7.5).

CHAPTER III

RESULTS

Characterizing Primary Ion

Figure 2 presents a full scan of projectiles (gray scan) conducted by increasing the electrostatic field on the Wien filter by 1 volt every 5 seconds (from 1v to 240v) with a constant magnetic field. This scan of projectiles corresponds to an extraction current of 20μA. Overlaying the scan are the average distribution of gold nanoparticles when the extraction current is set at 50μA(red) and 100μA(blue).

When the extraction current on the LMIS is set to 50μA the average size (n/q) of the gold nanoparticle emitted from the LMIS corresponds to n/q=100 (Au_{400}^{4+}). When increasing the extraction current to 100μA the average gold nanoparticle emitted corresponds to n/q=350 (Au_{2800}^{8+}).

By increasing the extraction current on the LMIS, larger droplets containing a greater number of constituent gold atoms, such as Au_{2800}^{8+} presented in this study, were selected by the Wien filter. This change allows for the shift in distribution of gold nanoparticles to higher masses. With this shift, one can select nano-projectiles ranging in much greater masses for nano-scale analysis.

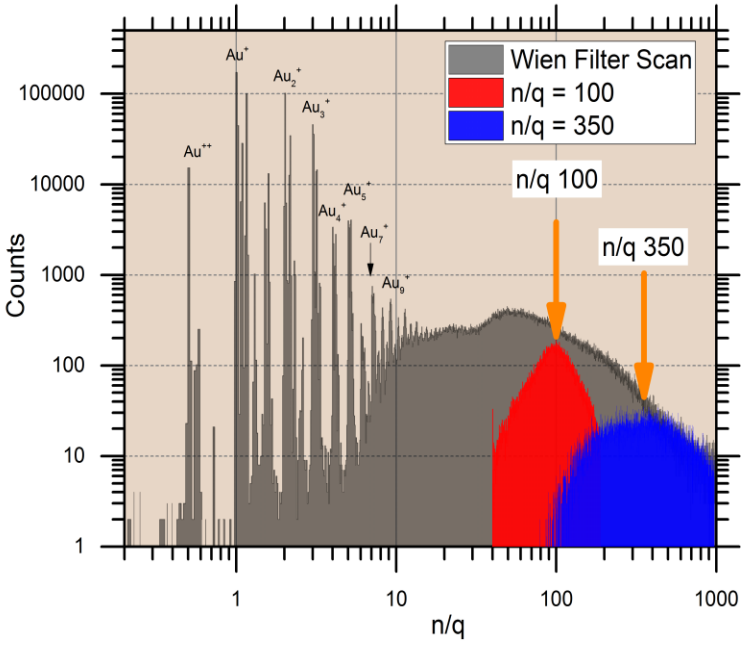

Figure 2. Scan of gold projectiles ranging from n/q=1 to n/q=1000 using a pulsar start and electron stop.

Nuclear Activation Analysis

Figure 3 presents mass spectra of 3 different sized projectiles that were implanted into HOPG for NAA. This was accomplished by using a pulsar start and electron stop. For each projectile that hits the HOPG an electron is emitted. By measuring the ToF between the pulsar and electron stop we are able to get a spectra of emitted electrons which corresponds to a distribution of projectiles implanted into the HOPG. Setting the parameters on the Wien filter allows the selection of the projectile using an appropriate window. When implanting n/q=100 projectile we found that the average projectile implanted into the HOPG corresponded more to n/q=114. Similarly, when implanting what we expected to be n/q=200 and 350, it was found from the distribution that the values correspond to 221 and 357 respectively. For the remainder of this paper I will denoted the mean distributions as 100,200, and 350 even though the distributions prove to have higher values then these.

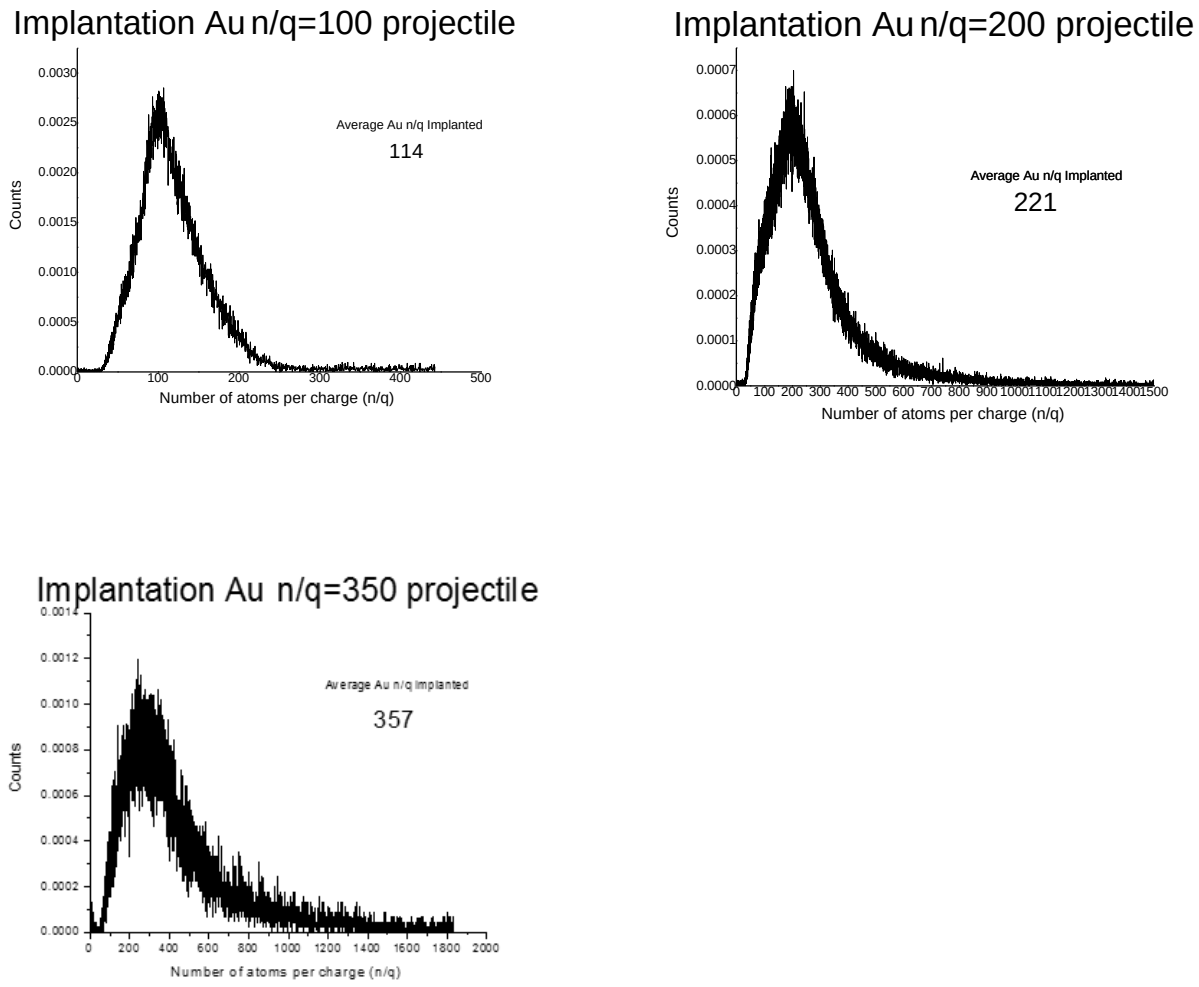

Figure 3. Scan of gold projectiles corresponding to average n/q values of 114, 221, 357

For the implantation of n/q=350, $1.17 * 10^9$ projectiles where implanted into the HOPG. NAA data was collected for n/q=350 in order to obtain the number of atoms that where implanted. relates the activity found from the NAA to the number of atoms that were implanted into the HOGP.

$$A = N_A \sigma_{AB} \Phi (1 - e^{-\lambda t}) \qquad \textbf{(1)}$$

Equation 1 where N_A is the number of atoms per cubic cm^2, σ_{AB} is the cross section, Φ is the number of neutrons per cm^2 per second, λ is the radioactive constant, and t is the half-life.

The NAA data collected resulted in 1200pg ± 400pg of implanted gold atoms. This value corresponds to 3100±1000 gold atoms. With the average n/q value resulting from the implantation and the number of gold atoms implanted found from the NAA data, we are able to determine the charge of the novel projectile. n/q=300 corresponds to an average charge of +8. The NAA data for n/q=100 and n/q=200 has not been collected yet.

Mass Spectra

Presented in Figure 4 is a negative mass spectrum of glycine bombarded with approximately $1X10^6$ clusters of 520keV Au_{400}^{4+}. In the lower mass range we find characteristic fragmentation from the molecular ion i.e. C-, CN-, CNO-, OCOH- , corresponding to m/z 12, 26, 42, 45 respectively. In larger mass ranges the deprotonated molecular ion (m/z 74) and the dimer (m/z 149) of glycine are found. Emission from the primary ion and gold-to-fragment recombination are present in ranges from (197 m/z to 240 m/z).

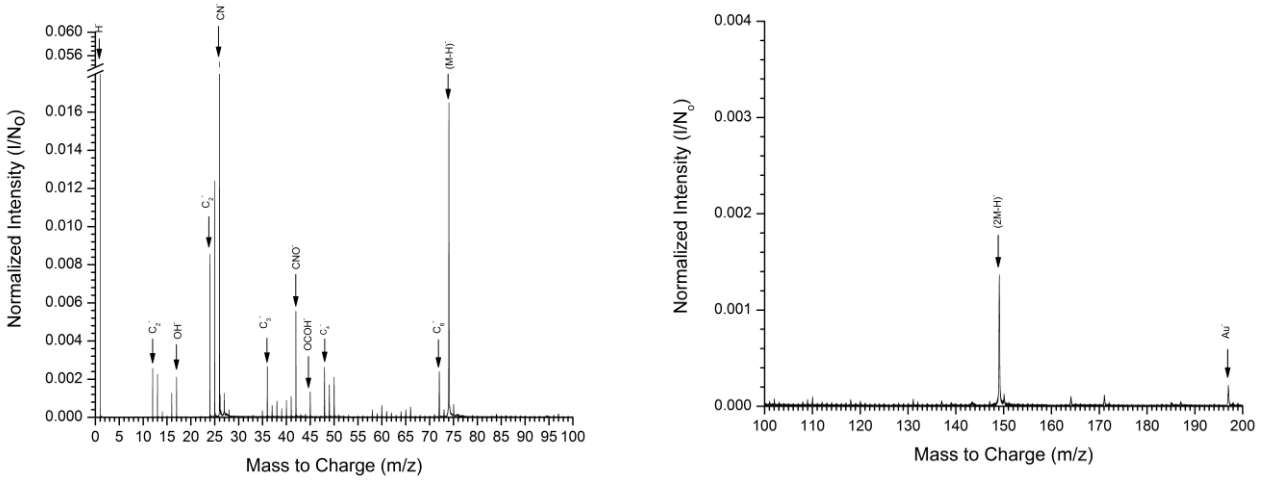

Figure 4. Mass spectra of glycine bombarded with 520keV Au_{400}^{4+}

Displayed in Figure 5 is a Mass spectrum of Gramicidin S bombarded with 1040 keV Au_{2800}^{8+}. The mass spectrum of Gramicidin S contains characteristic fragmentation in the lower mass ranges (1m/z to 150m/z) as well as fragmentation corresponding to amino acids found in Gramicidin e.g. leucine, proline, valine . We see a wide range of gold adducts e.g. $AuCN^-$, $Au(CN)_2^-$ ranging from m/z 200 to m/z 400. The deprotonated molecular ion and the molecular ion plus chorine is found in the higher mass ranges (1,139 and 1174 respectively) with astonishing intensities relative to the massive size of Gramicidin S.

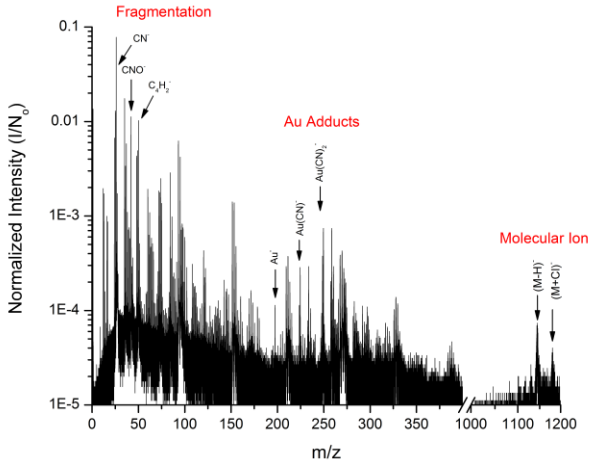

Figure 5. Mass spectra of Gramicidin S bombarded with 1040 keV Au_{2800}^{8+}

Secondary Ion Yields

Secondary Ion Yields for Glycine

Figure 6 shows the probability of obtaining a given number of secondary ions per impact when Glycine is bombarded with Au_{2800}^{8+} and Au_{400}^{4+}. From this data, using Equation 2, we can calculate the average number of secondary ions emitted per event for each projectile.

$$E[N] = \sum_{i=0}^{M} P(i) * i \qquad \textbf{(2)}$$

Equation 2: where i is the number of secondary ions emitted per event and $P(i)$ is the probability of emitting i number of secondary ions.

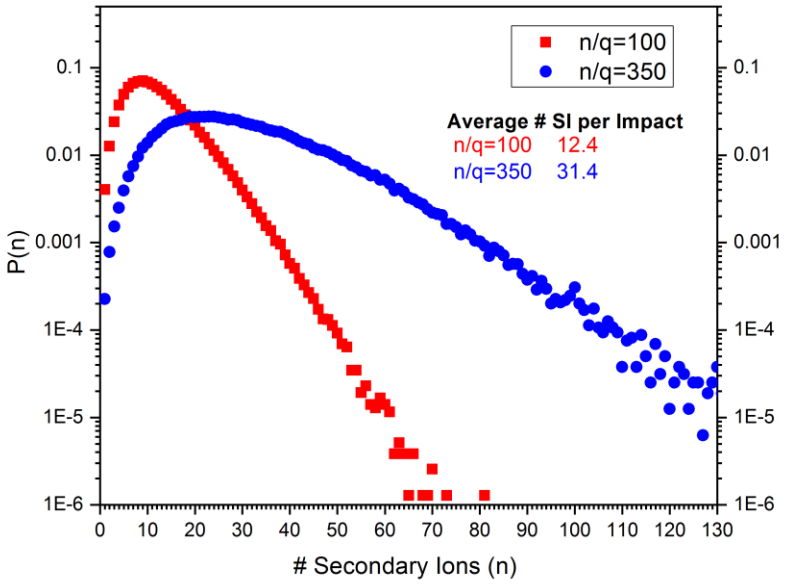

Figure 6. Secondary ion distributions of Glycine bombarded with 520 keV Au_{400}^{4+} and 1040 keV Au_{2800}^{8+}

When bombarding glycine with 520 keV Au_{400}^{4+} and 1040 keV Au_{2800}^{8+} we see an average emission of 12.4 and 31.4 secondary ions per event respectively. This corresponds to roughly 2.5x the emission from n/q=350 compared to n/q=100. To put this effect into prospective, we can take a look at the difference in probability for emitting 50 secondary ions per impact for both n/q=100 and n/q=350. The probability of emitting 80 SI per impact using n/q=100 is approximately 1E-4. The probability of emitting the same number of SI per impact using n/q=350 is 100 times more probable. A quantitative value of specific secondary ions emitted per impact can be measured using the equation:

$$Y_A = \sum_{i=0}^{n} \frac{I_A(i)}{N(i)} \quad \textbf{(3)}$$

Equation 3: where Y_A is the yield corresponding to ion A, I_A is the intensity of the selected ion and $N(i)$ is the number of impacts.

Figure 7 presents the secondary ion yields for Glycine bombarded with 520 keV Au_{400}^{4+} and 1040 keV Au_{2800}^{8+}. Comparing the yields, we see an increase in fragmented ions emitted from n/q=350; CN^-, CNO^-, and $OCOH^-$ having yields 1.1, 2.1, and 2 times greater than that of n/q=100 respectively. We see an $(M\text{-}H)^-$ increase from 1 to 2.8 when increasing the size of the projectile from n/q=100 to n/q=350. This effect is also seen in the dimer $(2M\text{-}H)^-$ having approximately a 390% increase when bombarding with this large novel projectile. These data confirm the enhancement of molecular emission over fragmentation when increasing the size of the projectile from Au_{400}^{4+} to Au_{2800}^{8+}.

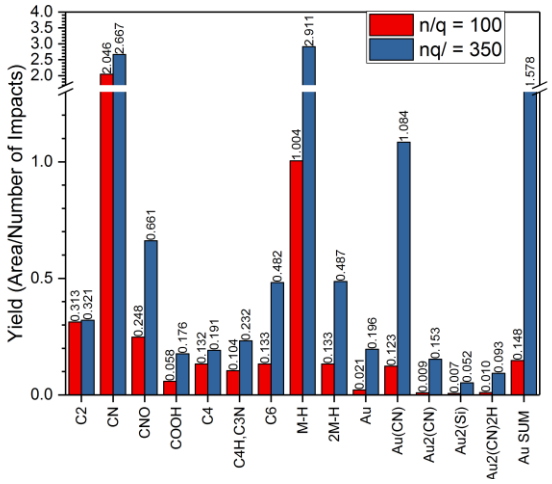

Figure 7. Secondary ion yields of glycine bombarded with 520 keV Au_{400}^{4+} 1040 keV Au_{2800}^{8+}.

Secondary Ion yields of Gramicidin S

Figure 8 shows the Secondary ion distribution when Gramicidin S is bombarded with $Au_{2800}^{8+}$and Au_{400}^{4+}. As previously discussed the expected value of secondary ions emitted per

impact can be calculated using equation 1. We find a similar trend with Gramicidin S as we did with glycine, n/q=350 having doubled the average secondary ions emitted per event of n/q=100 (40.2 and 18.2 respectively). To put this effect into prospective, we can take a look at the difference in probability for emitting 50 secondary ions per impact for both n/q=100 and n/q=350. The probability of emitting 50 SI per impact using n/q=100 is approximately 1E-4. The probability of emitting the same number of SI per impact using n/q=350 is .01, being 100X more probable then n/q=100.

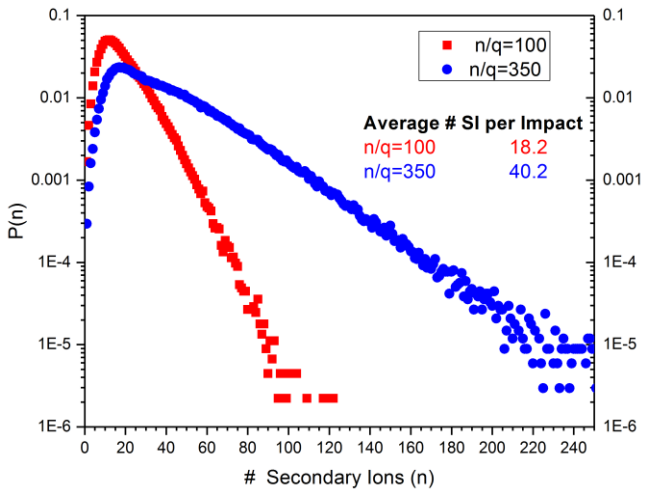

Figure 8. Secondary ion distributions of Gramicidin S bombarded with 520 keV Au_{400}^{4+} and 1040 keV Au_{2800}^{8+}.

Figure 9 presents the secondary ion yields (calculated using equation 2) for Gramicidin S bombarded with 520 keV Au_{400}^{4+} and 1040 keV Au_{2800}^{8+}. The trend of secondary ion yields of Gramicidin S present results that mirror that of glycine. From the data we see a jump in yield when using n/q100 and n/q=350 of CN^- and CNO^- from 2.2 to 2.6 and .45 to .85 respectively. In this sample, we also see an increase in yield of $(M-H)^-$ from .2% to .3% when increasing the size of the projectile from n/q=100 to n/q=350.

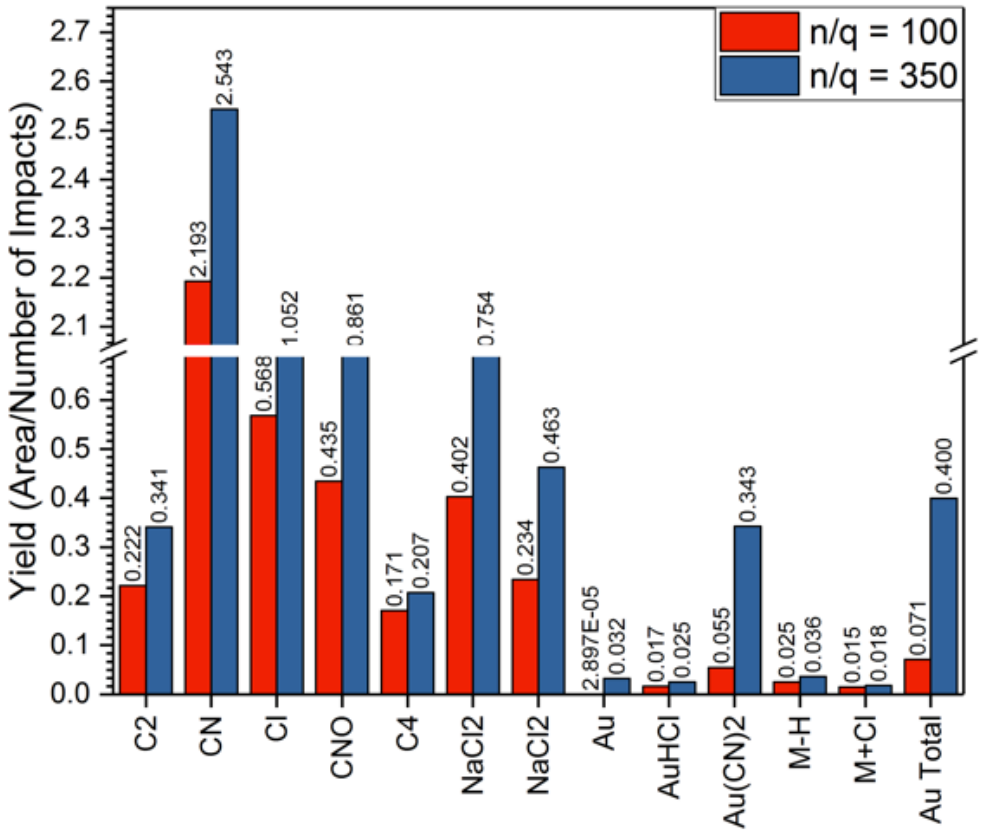

Figure 9. Secondary ion yields of Gramicidin S bombarded with 520 keV Au_{400}^{4+} and 1040 keV Au_{2800}^{8+}

Gramicidin and Glycine where bombarded with n/q=200 projectile, but a discrepancy was found when analyzing the data for this specific projectile. There appeared to be an increase of yield in Glycine when bombarding n/q=100 versus the larger projectile n/q=200, but when analyzing the data for Gramicidin, the yield appeared to be the same for both projectiles. When conducting the experiment for n/q=200 on gramicidin, there was a fluctuation of "counts", meaning that the source was not stable. With the source being unstable, the number of projectiles, n/q=200, hitting the sample is limited, which in turn gives rise to less events. This could be a plausible explanation as to why the data does not agree with previously observed trends. This experiment will be attempted again in order to obtain consistent results for nq=200.

CHAPTER IV

CONCLUSION

By increasing the extraction current of the LMIS we can promote the emission of larger projectiles up to n/q=350. NAA is a useful tool for characterizing these novel projectiles. By implanting n/q=350 into HOPG and performing NAA on our sample, it was determined that the average number of gold atoms per each cluster corresponds to 3100±1000 gold atoms and an average charge of +8.

These nano projectiles can increase the secondary ion yield from a sample substantially. When comparing the average secondary ions emitted per impact from gold Au_{2800}^{8+} to Au_{400}^{4+} we see roughly double the ions emitted from Au_{2800}^{8+} in both gramicidin and glycine. Glycine when bombarded with Au_{2800}^{8+} projectile showed promising results, n/q=350 having an average of 2.8 deprotonated molecular ions emitted per event and n/q=100 having approximately 1.0.

With higher molecular ion yields one can characterize surfaces by performing surface/depth analysis with higher sensitivity. Furthermore this novel nano projectile can measure co-emitted molecules for enhanced surface homogeneity tests at the nano scale.

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