

PRF #58113-DNI6

Project Title: Characterization of a Solution-Cathode Glow Discharge Source for Ionization, Tunable Fragmentation, and Rapid Identification of Molecules and Polymers with Mass Spectrometry

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The second year of this project focused on the ionization processes and fragmentation pathways occurring within the solution cathode glow discharge (SCGD) ionization source. First by analysis of analytes that undergo different ionization mechanisms than those previously analyzed. And second by observing the internal energy distribution curves for two different types of thermometer molecules. Small molecule analysis of pesticides in the first year of the project indicated that SCGD-MS was useful for small molecules that undergo proton-transfer ionization and are detected as positive ions. To broaden the scope of the SCGD-MS method for small molecules analysis was conducted on explosive samples that are more likely to undergo ionization via adduct formation and are often detected as negative ions. Detection and ionization of two common explosives, TNT and RDX, were obtained with SCGD-MS in negative-ion mode. Ionization and detection of negative ions were achieved within the SCGD source without the need for a change in polarity or reversal of the electrodes. Figures- of-merit were also carried out for the explosive samples and resulted in LOD of 34 ppb (170 pg) for TNT and 16 ppb (80 pg) for RDX with samples in solution. Ambient desorption ionization mode (ADI) of SCGD source was found to have higher signal and less chemical background for the explosive samples. Figure 1 shows the mass spectra for RDX and TNT when analyzed with SCGD in the ADI mode. The enhancement in ion signal in ADI-mode is a result of the analytes being able better undergo the preferred adduct formation ionization pathway. Better LOD may be achieved with ADI-mode but would be challenging to quantify. Further studies to determine why explosive samples had decreased ionization in solution compared to ADI are necessary. With further improvements, the SCGD-MS method could be beneficial for the detection of trace amounts of explosives in a variety of samples, including water and soil. Conclusively, the technique of SCGD-MS can be used for trace detection of pesticides and explosives in solution and has the potential for broader application to samples containing these and other small molecules of interest.

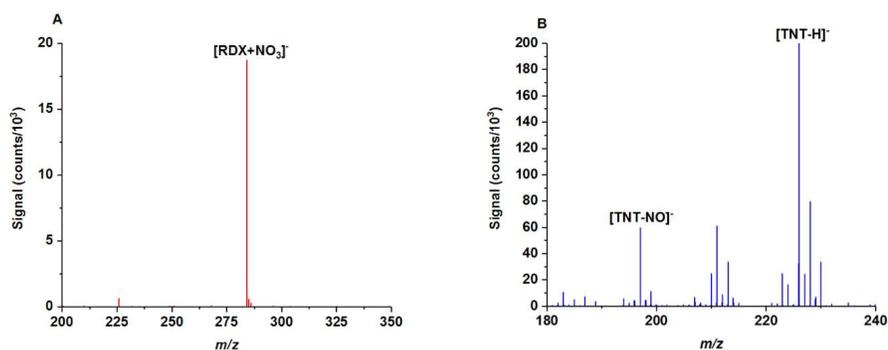


Figure 1. Mass spectra for RDX (A) and TNT (B) when analyzed with SCGD-MS in ambient desorption ionization (ADI) mode.

An investigation of the differences in internal energy distribution for two types of thermometer molecules, substituted benzylamines and benzylpyridinium salts, was conducted with SCGD-MS. Thermometer molecules are characterized by their predictable fragmentation and low bond dissociation energies. Due to the differences in preferred ionization and volatility, a comparison of these thermometer molecules provided more information on whether both types were useful as internal energy gauges for specific ionization pathways occurring within the SCGD source. Internal energy distribution curves were determined by calculation of the survival yield of the substituted thermometer ions. The survival yield of each molecule was plotted against the bond dissociation energy to establish a breakdown curve and the internal energy distribution was calculated from the breakdown curve.

Consistent ion signal for benzylamines was seen across a wide discharge current range with the highest signal achieved at 65 mA and above. Benzylamines ionize by protonation of basic sites, which can be achieved by ESI and APCI mechanisms. The APCI-like ionization is favored due to higher abundance of gaseous protons from the glow discharge and because the mechanism occurs at a faster rate. The internal energy distributions for the benzylamine thermometer ions were found to change with variation in discharge

currents. Larger average energies and narrower internal energy distributions for benzylamines were found to be more indicative of the occurrence of APCI-like processes and were observed with SCGD currents above 55 mA. Figure 2 shows the internal energy distributions at currents of 35, 55 and 65 mA. The discharge current of 55 mA was found to be a transition in internal energy distributions with about 55 mA favoring APCI-like ionization. The observed internal energy distribution curves for the benzylamines showed that analytes that can undergo multiple ionization pathways are affected by the source parameters.

Unlike the benzylamines, significant ion signal for the substituted benzylpyridiniums was only achieved at discharge currents higher than 60 mA. This result correlates with previous findings that analytes that favor ESI-like ionization from Taylor cones formed on the cathode surface have higher molecular ion signal at higher discharge currents. Due to low volatility and ionic charge, benzylpyridiniums are unable to undergo chemical ionization, and so ionize only by ESI mechanisms. These same results were confirmed when both benzylamine and benzylpyridinium internal energy distributions from SCGD-MS were compared to the internal energy curves from analysis with ESI-MS. The parameters of SCGD were also shown to have an effect on the internal energy imparted on the ions within the source. A shift of 0.3 eV to the average internal energy was observed when methanol was used as the sample carrier solution in comparison to water, most likely due in part to increase thermal energy within the source (*cf.* Figure 3). A shift to higher internal energies was also observed for benzylamines with an increase in the discharge current. Both of these observed changes to the internal energy correlate to parameters in which the abundance of fragment ions increases. The analysis of the internal energy distribution curves demonstrated that multiple ionization pathways are occurring within the SCGD. Analytes capable of undergoing ionization by more than one pathway such as the benzylamines exhibited internal energy distribution curves that indicate a combination of both pathways at specific SCGD parameters, namely higher discharge currents. Other source parameters also affected the internal energy curves including change in the discharge support solution by addition of methanol. Future work will continue to focus on the ionization mechanisms and fragmentation pathways observed in the SCGD including ionization by adduct formation as observed with the explosive analytes.

In addition, ACS PRF funds have had a notable impact on the PI and students working on this project. The graduate student on the project, Courtney Walton, successfully defended her PhD dissertation in August 2019 and much of her dissertation work came from this project; it is anticipated that at least 3 manuscripts will be submitted soon for her efforts. In addition, she presented a lecture at the 2018 SciX conference (invited), 2019 Northeast Regional ACS meeting (invited), 2019 Pittsburgh Conference, and the 2019 American Society for Mass Spectrometry (ASMS) conference. She was also recognized by the local ACS section as an Emerging Leader in Chemistry. Jessica Hellinger, one undergraduate funded by this project, was awarded undergraduate researcher awards from both the Society for Applied Spectroscopy and the Eastern Analytical Symposium for this work. Another undergraduate, Judy Wu, presented an oral presentation from this work at the 2019 Pittcon, won the Best Research prize at the 2019 RPI Undergraduate Research Symposium and has graduated with her BS in Chemistry. The PI of the project has presented this work at eight invited lectures at national and international conferences over the project year.

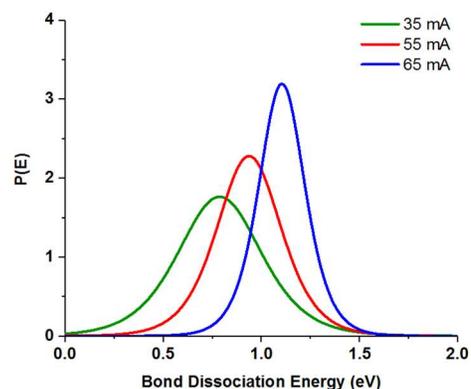


Figure 2. Internal energy distribution curves for benzylamine thermometer ions for different SCGD currents.

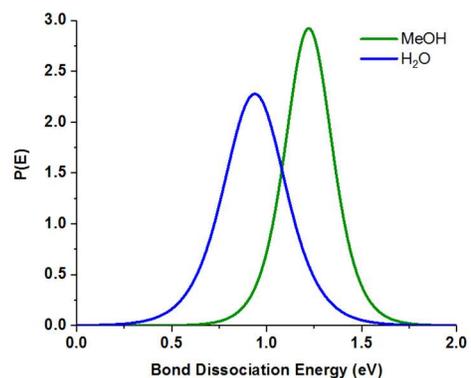


Figure 3. Internal energy distribution curves for benzylamine thermometer ions with sample carrier solution of 100% water (red) and 100% methanol (blue).