

Coupling of a Liquid Sampling – Atmospheric Pressure Glow Discharge (LS-APGD) Microplasma with a Commercial Triple-Quadrupole Mass Spectrometer

Tyler Williams¹ and R. Kenneth Marcus¹

¹Clemson University, Department of Chemistry, Clemson, SC 29634



Introduction

ICP-MS has long been considered the gold standard for elemental analysis. Many of the issues that have plagued ICP-MS, such as spectral interferences, have largely been resolved with the introduction of multiple quadrupole ICP-MS instruments.¹ Recently, use of triple-quadrupole geometries has allowed for numerous scanning methods to be used with can help to remove interferences and other concomitant ions.²

The liquid sampling – atmospheric pressure glow discharge (LS-APGD) has been developed as a versatile excitation/ionization source for optical emission spectroscopy and mass spectrometry. Through its development as an ionization source, it has primarily been coupled to trapping type mass spectrometers. These instruments have neither the mass range nor the MS/MS options that can be found on a commercial triple-quadrupole mass spectrometers.

Here, a Thermo Scientific TSQ Quantum Access MAX triple-quadrupole mass spectrometer, typically equipped with an electrospray ionization source, has been outfitted with the LS-APGD. This instrument has the ability to perform both precursor and product ion scans, as well as the ability to look at neutral losses. Through the use of these scanning modes, not only can a wide breadth of information be obtained, but a more in-depth look at the plasma chemistry can be observed. Ultimately, of course, enhanced performance relative to single-quad instruments is expected.

Apparatus

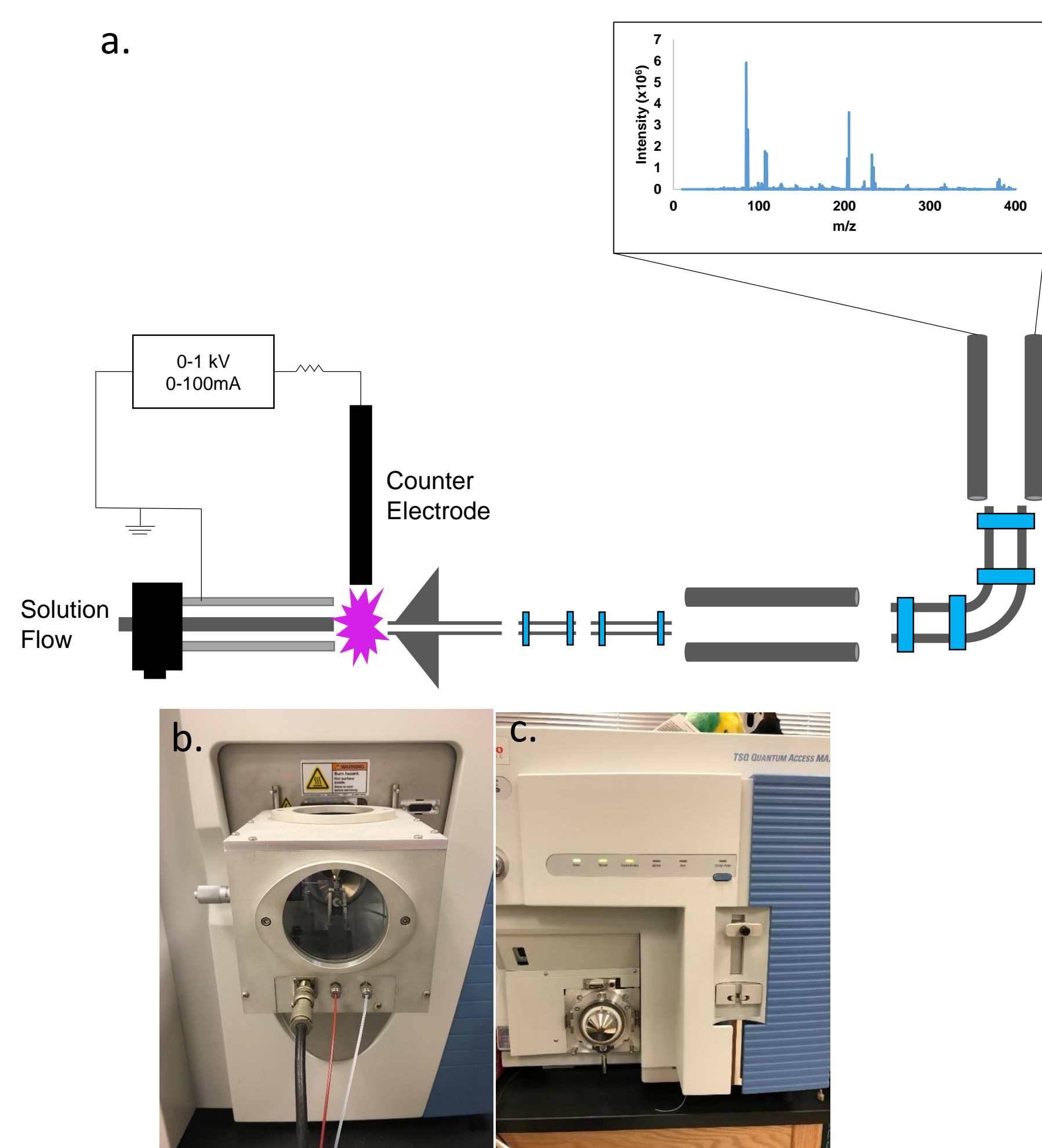


Figure 1: a) Diagram of the LS-APGD-QqQ system b) LS-APGD source c) Thermo Scientific TSQ Quantum Access MAX

The LS-APGD system is composed of two electrodes: an electrolytic solution and a metal counter electrode. The electrolytic solution is introduced through a fused silica capillary that is housed within a stainless steel outer capillary. A helium sheath gas flows between the capillaries at 0.2 L min⁻¹. The plasma is sustained by a 2% (v/v) HNO₃ solution delivered via a syringe pump at 25 μL min⁻¹. The system is powered by a d.c. power supply operating a 30 mA.

Results and Discussion

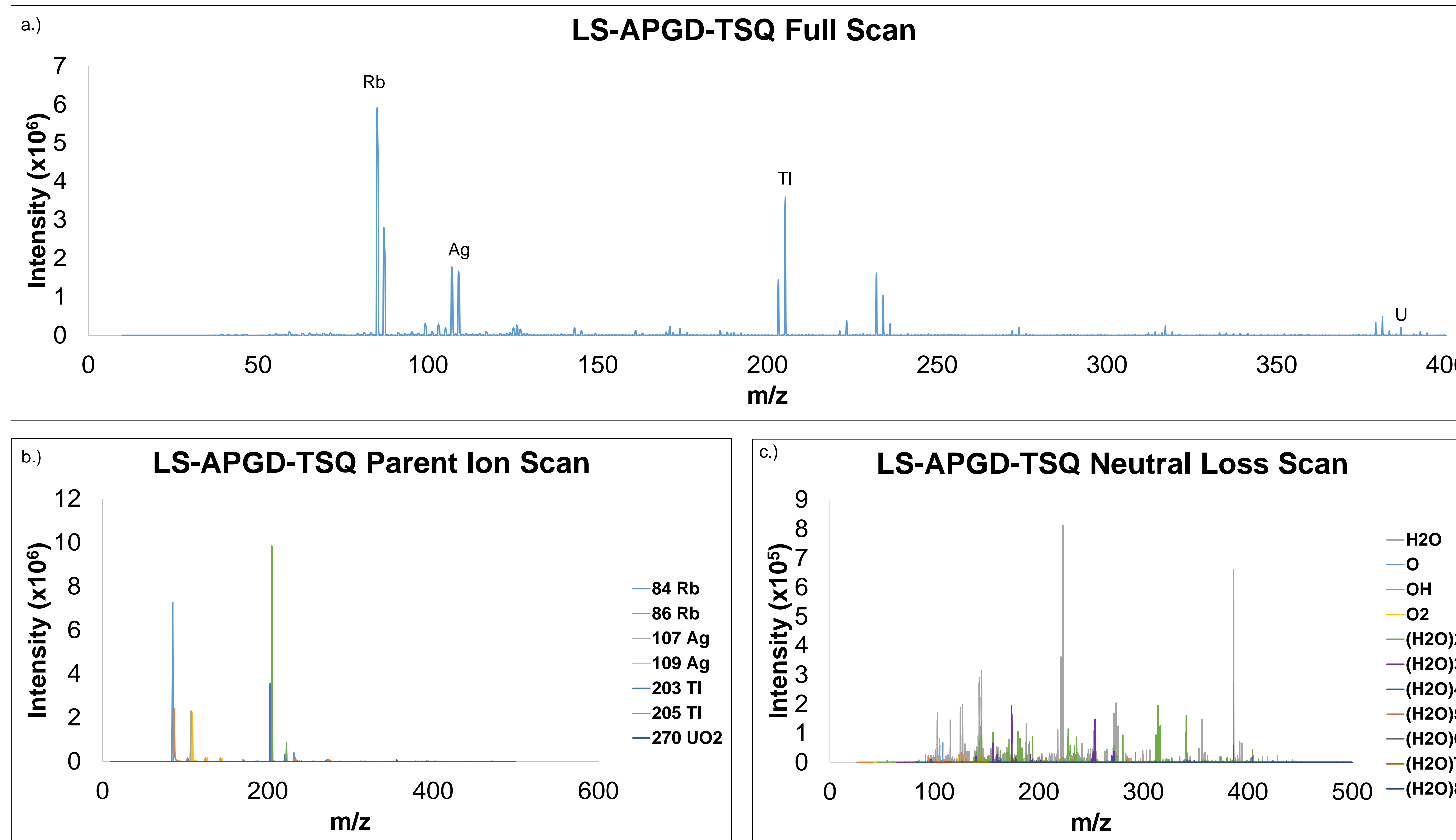


Figure 2: 50 μg mL⁻¹ solution containing Rb, Ag, Tl, and U analyzed using a) full, b) parent ion, and c) neutral loss scan modes.

Figure 2a shows the spectrum of a multi-element solution obtained through a full scan. In this spectrum, peaks for the four test elements are easily observed. In addition to these peaks, numerous lower intensity peaks can be seen throughout the spectrum. Using the available scanning modes of the TSQ, these peaks can be further studied. In Fig. 2b, a parent ion scan is shown. This method scanned from 0-500 m/z the find any peaks that would fragment into the masses of the analytes in the sample. From this scan, it can be seen that primarily Ag and Tl are forming oxides. In Fig. 2c, a neutral loss scan is shown. Here the instrument scanned across 10-500 m/z looking for a loss of a number of different species. Most commonly lost were oxygens, hydroxides, and small water clusters.

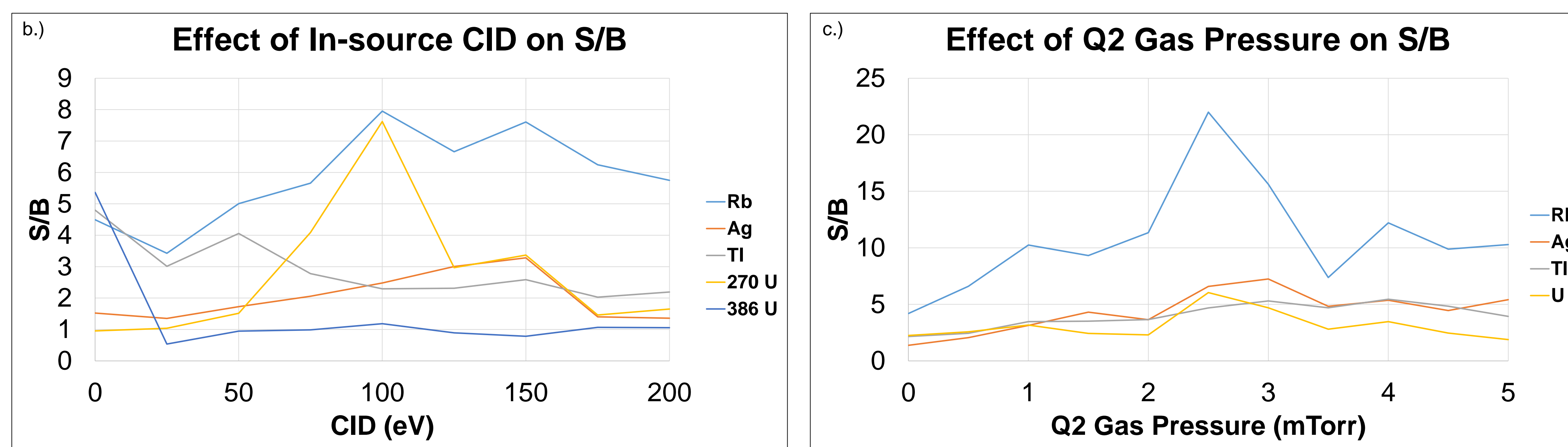


Figure 3: Signal-to-background ratio of a 5 μg mL⁻¹ solution monitored as the a) in-source CID energy and b) Q2 gas pressure were varied

By varying the in source CID energetics, a general increase in the S/B ratio can be seen. An exception to this can be seen with Tl which undergoes a slight decrease which may suggest an interfering ion. Another major advantage to the triple-quadrupole is the availability to add a collisional gas into the second quadrupole in a controlled fashion. As the pressure of the Q2 is increased, a slight increase in S/B can be seen, especially in the case of rubidium. The increase in gas pressure is likely slowing down the ions and more collisions with this gas cause a reduction in background ions without affecting the analyte signal.

Conclusion

This coupling of the LS-APGD with a commercial triple quadrupole mass spectrometer, normally sold towards proteomics applications, shows great potential. Utilizing the numerous scanning methods, a greater depth of information can be obtained from a sample. The product ion scan shows what peaks contain an ion of interest while the neutral loss scan can show what adducts are present across the spectrum.

Future studies with this system can open up various new applications. Using a neutral loss scan and a precursor ion scan, the types of background ions present in the system can be identified. This may help in shed light on the chemistry occurring within the plasma.

In addition, using optimized conditions from Fig. 3, a simultaneous multi-element calibration was performed. All four elements and their isotopes could be simultaneously monitored using selected ion monitoring and preliminary LODs in the low ppb range were obtained for all four elements.

Table 1: LODs obtained from a simultaneous multi-element calibration

Element	R ²	LOD
Rb	0.9866	53 ng mL ⁻¹
Ag	0.9527	57 ng mL ⁻¹
Tl	0.9876	3.1 ng mL ⁻¹
U	0.9753	61 ng mL ⁻¹

Future Work

- Further characterization of the species seen in the neutral loss scan and relative to fundamental gas-phase chemistry
- Kinetic energy discrimination experiments³
- Optimization of analytically-relevant operation conditions

References

- 1) Rousis, N.I.; Thomaidis, N.S.; Talanta. 2017. 175. 69-76
- 2) Bolea-Fernandez, E.; Balcaen, L.; Resano, M.; Vanhaecke, F.; J. Anal. At. Spectrom. 2017. 32. 1660-1679
- 3) Yamada, N.; Spectrochim. Acta. B 100. 2015. 31-44

Acknowledgements

This work was supported by the Defense Threat Reduction Agency, Basic Research Award #HDTRA1-14-1-0010, to Clemson University