

Supplementary Information

for

**Coupling of the liquid sampling – atmospheric pressure glow
discharge (LS-APGD) ionization source with a commercial triple
quadrupole mass spectrometer**

Tyler J. Williams and R. Kenneth Marcus*

Clemson University, Department of Chemistry, Clemson, SC 29634

Optimization of In-Source CID Energy and Q2 Gas Pressure

To optimize these aspects, 50 μL injections of the 10 $\mu\text{g mL}^{-1}$ multi-element solution were performed, with the resulting S/B ratio for each analyte computed and used as the test metric. Triplicate injections were performed while varying the in-source CID 0 – 200 V in 25 V increments (with no CID occurring in Q2). After optimization, the same was done for the Q2 gas, varying the pressure from 0 – 5 mTorr at 0.5 mTorr increments.

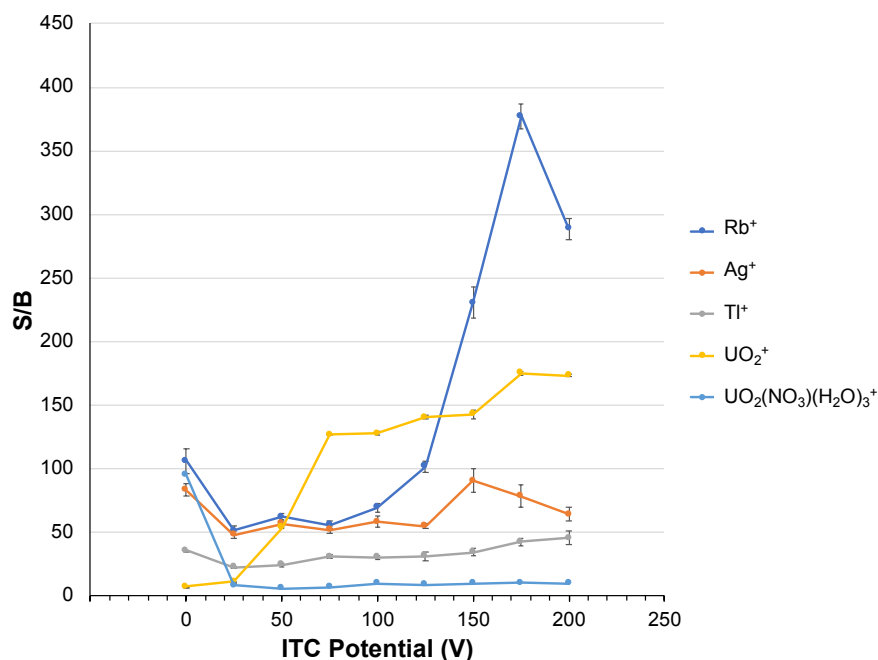


Figure S1. Effect of ion transfer capillary potential on the S/B of the multi-element solution. Each point represents the average S/B of triplicate injections. Discharge conditions were those presented in Table 1. Analyte concentrations = 10 $\mu\text{g mL}^{-1}$ (each), target analyte isotopes: ^{85}Rb , ^{107}Ag , ^{205}Tl , and $^{238}\text{U}^{16}\text{O}_2$.

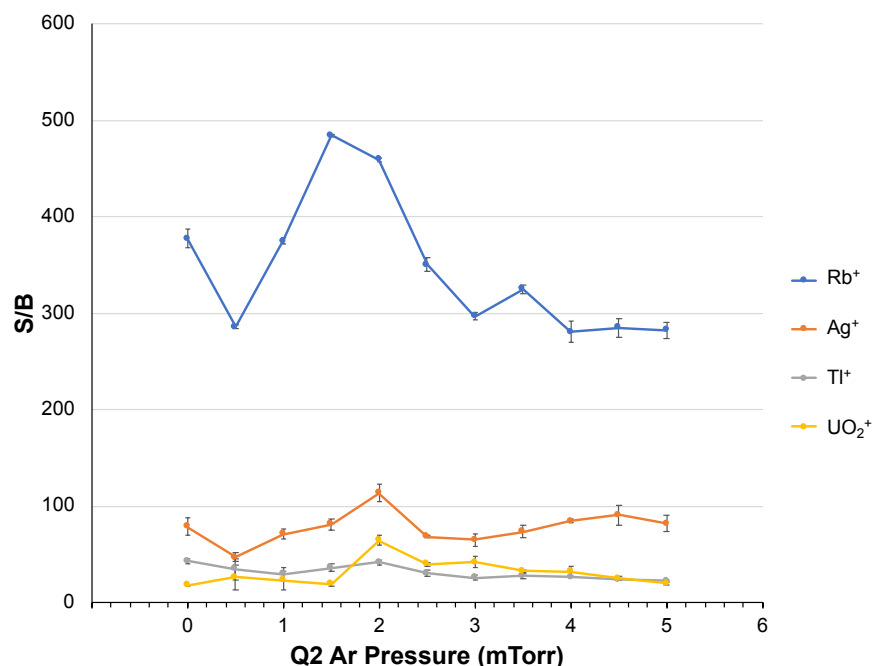


Figure S2. Effect of the argon pressure in Q2 on the S/B ratios of the multi-element solution. Each point represents the average S/B of triplicate injections. Discharge conditions were those presented in Table 1. Analyte concentrations = 10 $\mu\text{g mL}^{-1}$ (each), target analyte isotopes: ^{85}Rb , ^{107}Ag , ^{205}Tl , and $^{238}\text{U}^{16}\text{O}_2$.

Optimization of MS/MS Conditions

The maximum values in the chromatograms are expected to be the point in which optimum fragmentation occurs to yield the analyte species. Seen in Fig. S3a, a maximum yield with respect to the collision energy is found at 25 V for each of the analyte species. The response reflects greater levels of efficiency with increasing voltage, followed by ion losses (scattering) due to excess kinetic energies. In Fig. S3b, there is no clear, universal optimum in the Q2 gas pressure. Detailed interrogation across the individual spectra suggested that the greatest spectral clarity relative to the background water-related ions was obtained at a Q2 cell pressure of 1.5 mTorr Ar. Thus, a Q2 bias of 25 V and pressure of 1.5 mTorr Ar was used through the remainder of the present studies.

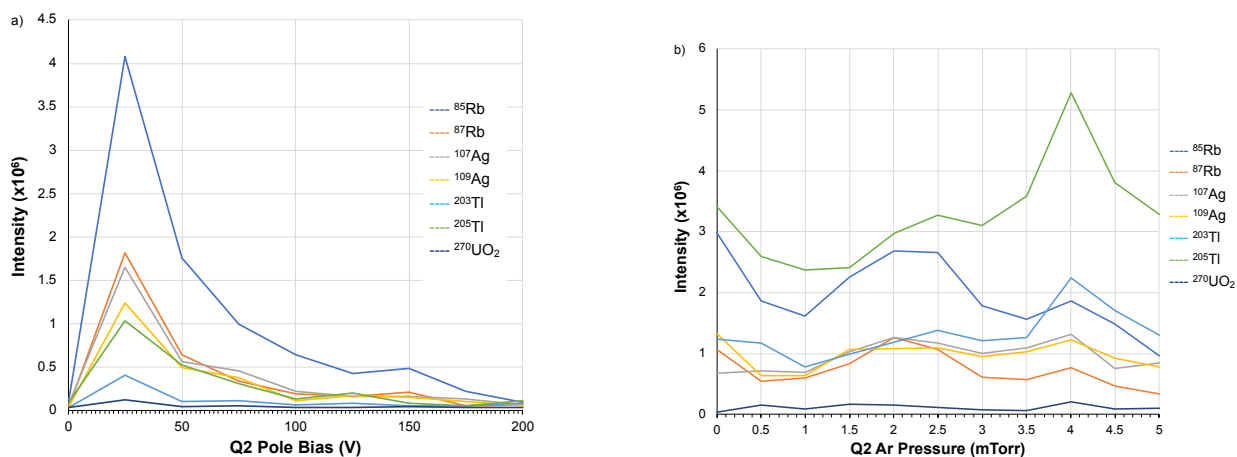


Figure S3. Effects of the a) Q2 pole bias and b) Q2 Ar pressure on the extracted ion chromatogram of each analyte isotope for a 25 $\mu\text{g mL}^{-1}$ solution containing Rb, Ag, Tl, and U. Discharge conditions were those presented in Table 1.

To optimize the neutral loss information content, the collisional energy was increased in 25 V increments and the total ion chromatogram (TIC) was monitored to find the point where the ion response was the most intense. The same was done for the Q2 gas pressure, increasing in 0.5 mTorr increments, and finding the maximum in the TIC. Points past the maximum may undergo increased degrees of fragmentation resulting in species losses of greater mass (e.g., a second H₂O molecule) than the defined mass. The results of these studies are seen in Figs. S4 and S5, showing maximum responses at 25 V pole bias and 0.5 mTorr Ar.

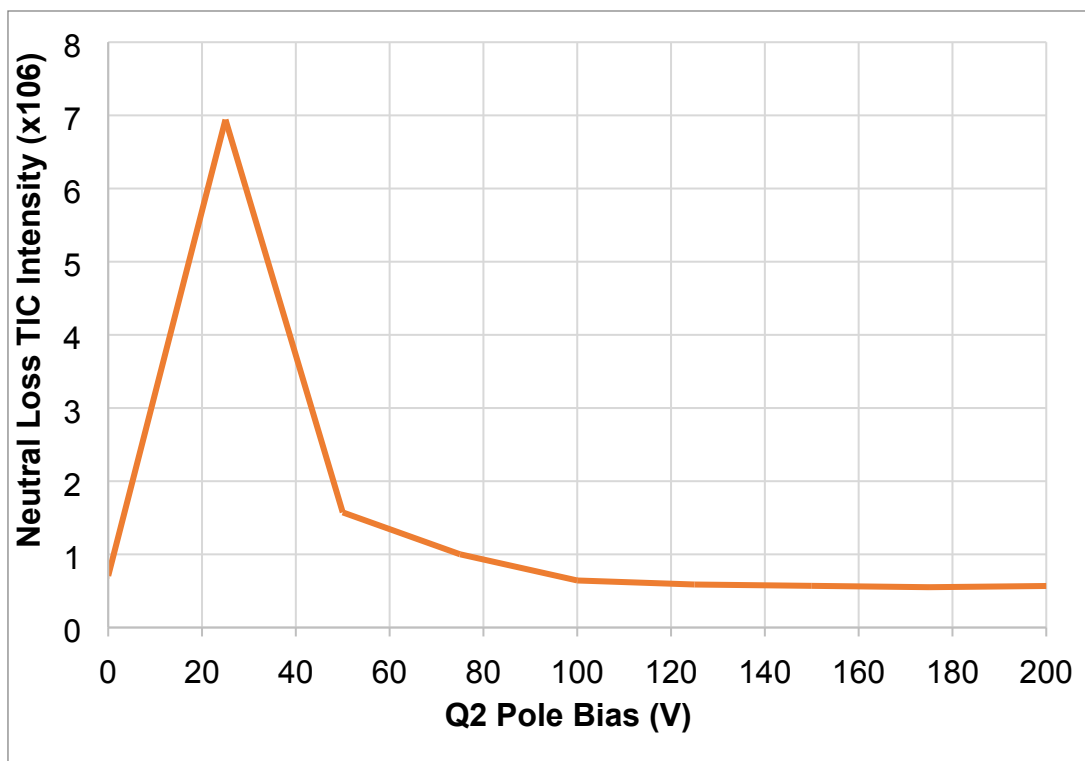


Figure S4: Effect of Q2 collisional energy on the intensity of the total ion chromatogram for a neutral loss scan of a 25 $\mu\text{g mL}^{-1}$ solution containing Rb, Ag, Tl, and U.

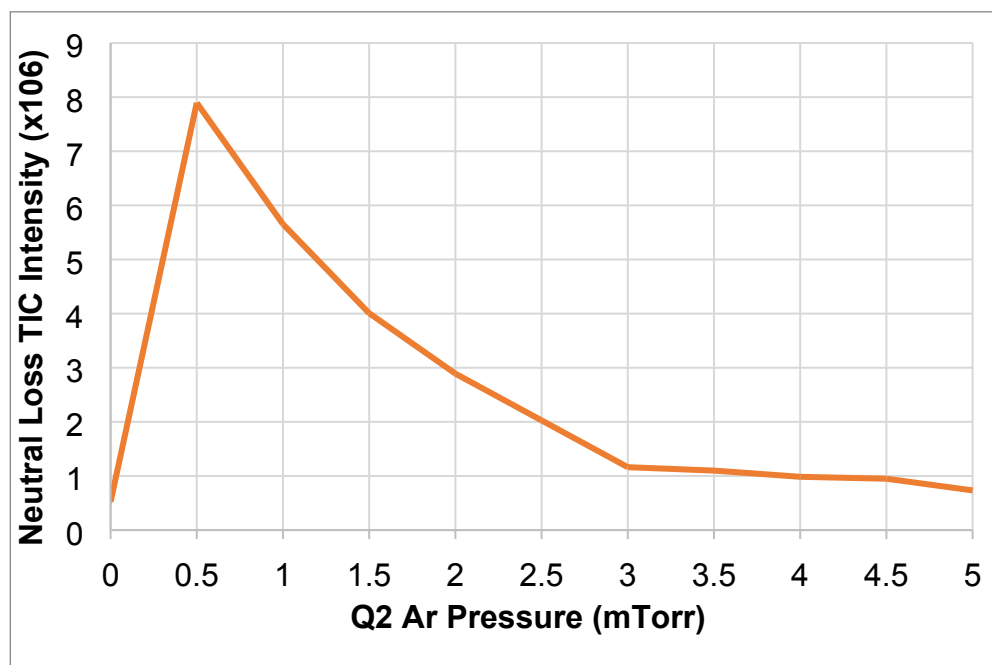


Figure S5: Effect of Q2 gas pressure on the intensity of the total ion chromatogram for a neutral loss scan of a 25 $\mu\text{g mL}^{-1}$ solution containing Rb, Ag, Tl, and U.