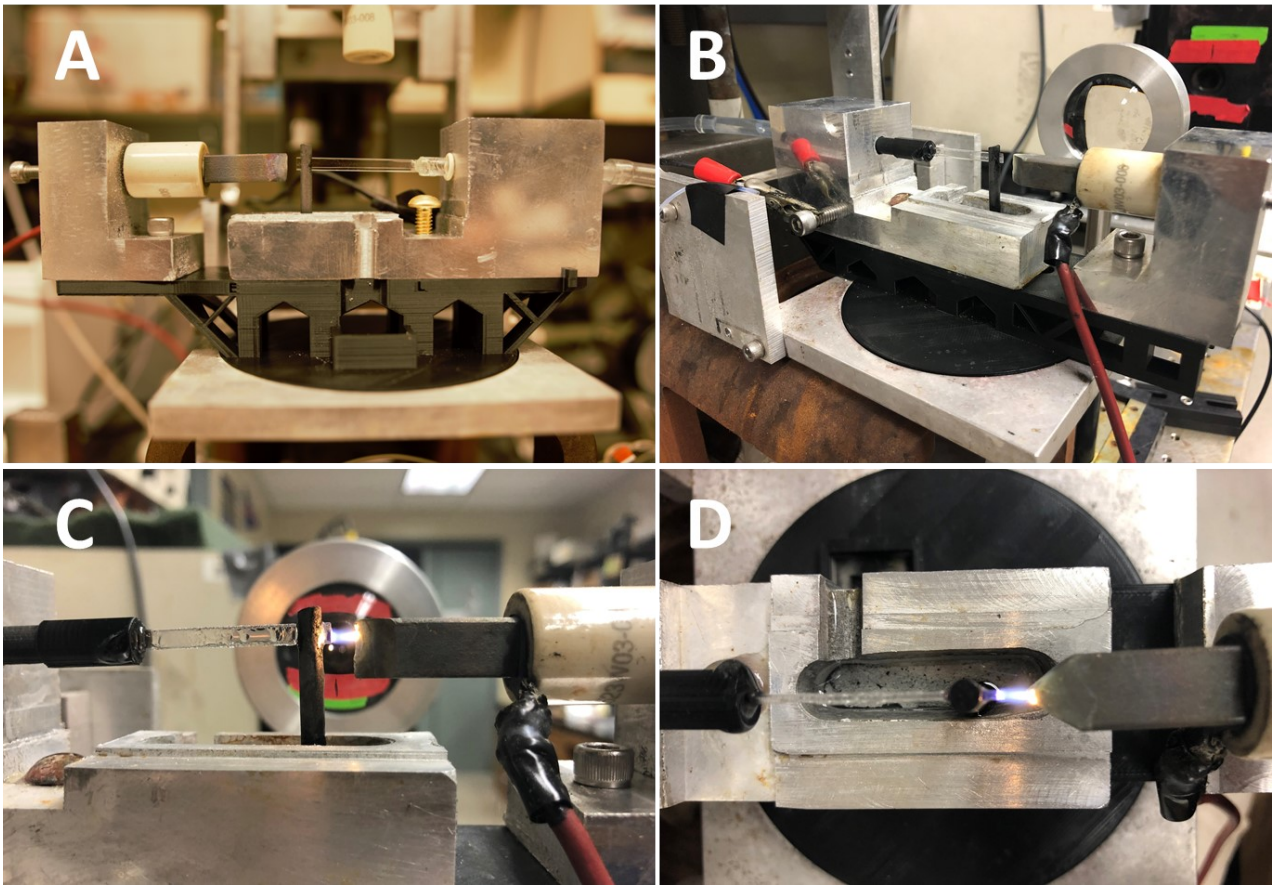
Electronic Supplementary Material (ESI) for Journal of Analytical Atomic Spectrometry.

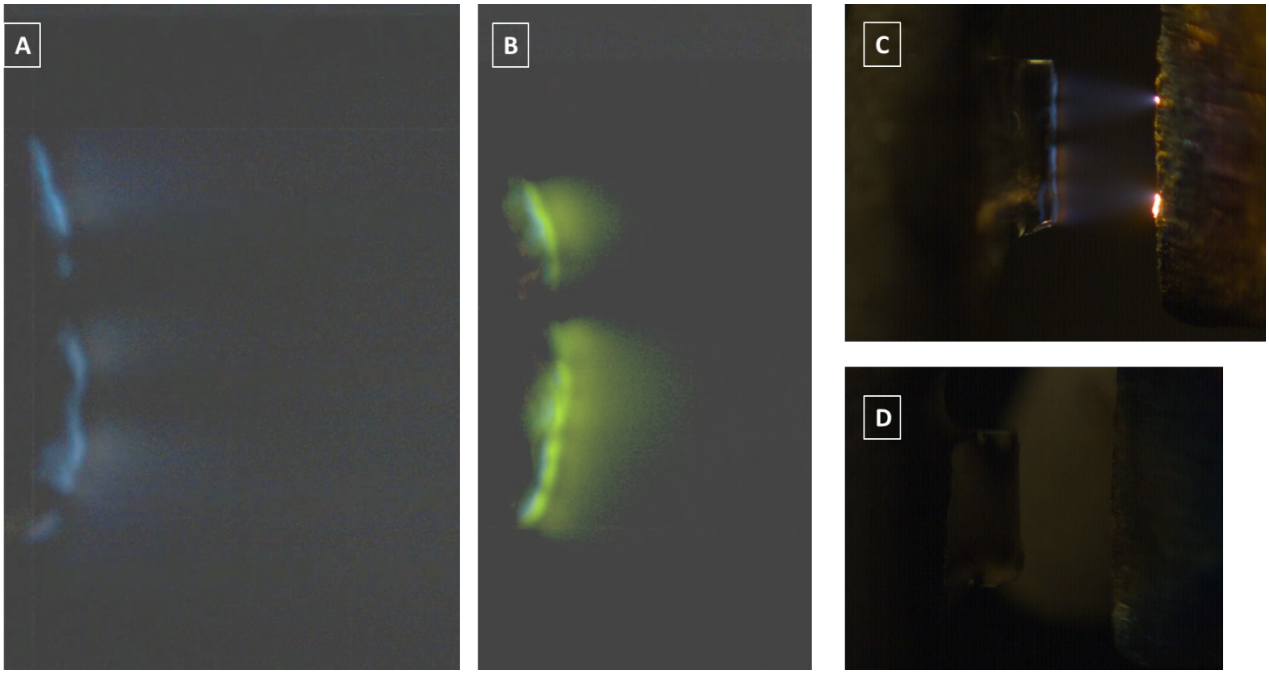

# Supplemental Figures

## Supplemental Figure 1




**Supplemental Figure 1:** Pictures of the horizontal SCGD experimental setup. **A**. Side on view with plasma off. Original glass holder for rectangular capillary used here. **B**. Side on view with plasma off with lens in place for experiments. **C**. Side on view with plasma on. **D**. Viewed from above, plasma on.

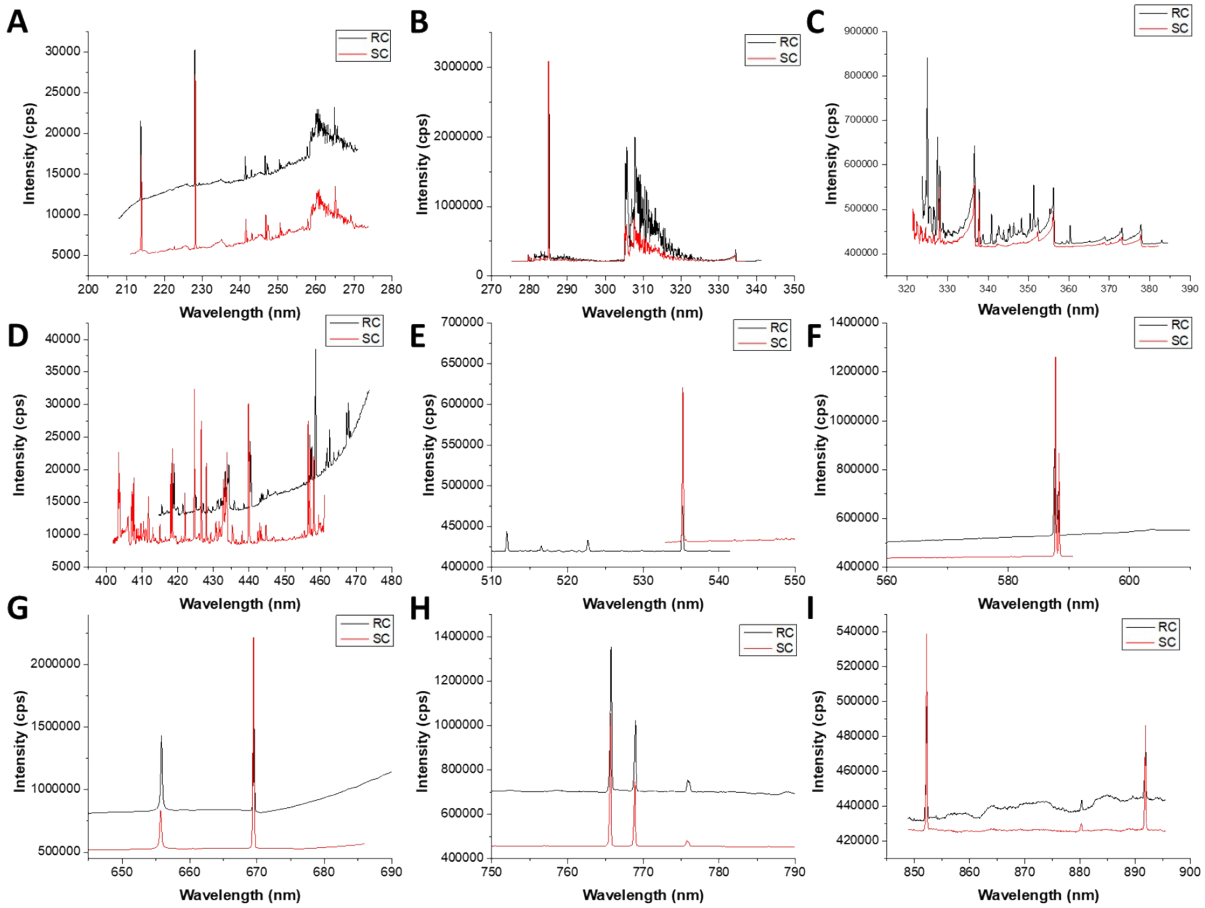
**Supplemental Figure 2**




**Supplemental Figure 2:** High speed videos. A) 5000fps, 3mm gap, 3mL/min, 80mA, 0.1M $HNO_3$ only. B) 5000fps, 3mm gap, 3mL/min, 80mA, 10mg/L Tl. C) C) 1000fps, 3mm gap, 3mL/min, 80mA, 0.1M $HNO_3$ only. A) 1000fps, 3mm gap, 3mL/min, 80mA, 0.1M $HNO_3$ only, showing plasma ignition.

**Supplemental Figure 3**

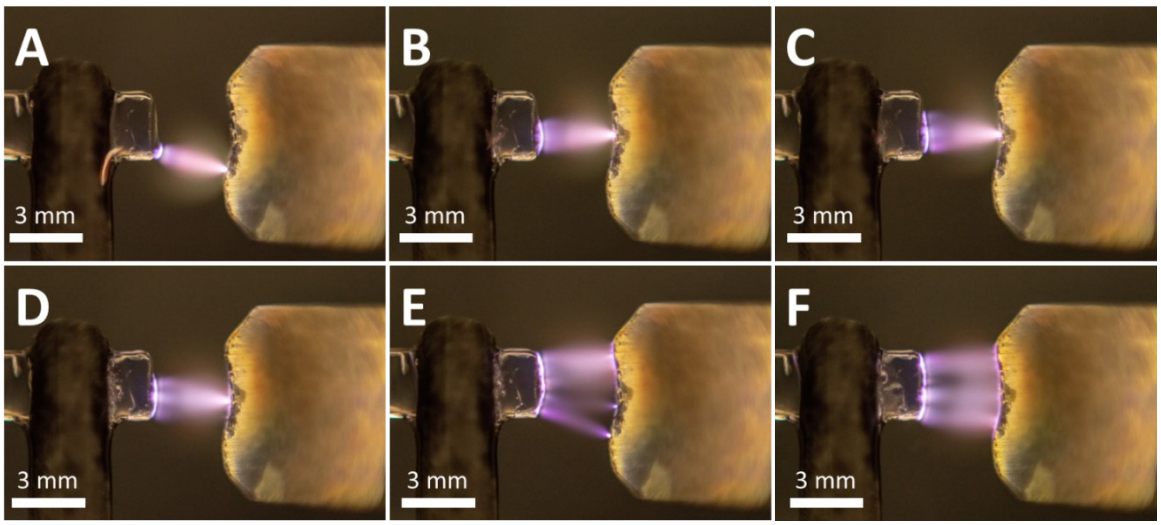

**Supplemental Figure 3:** Pictures of the SCGD studying several elements; 0.1M $HNO_3$, Y, Tl, In, Li




**Supplemental Figure 4**

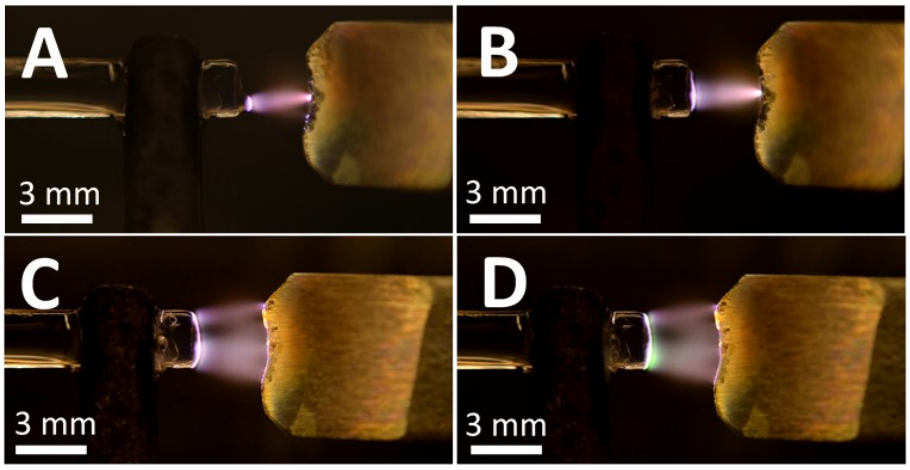
**Supplemental Figure 4:** Spectra of equal concentrations of various elements analyzed with the RC and the SC. In each spectrum, the element being analyzed was the same concentration. Acquisition settings and plasma settings were exactly the same. The only change in conditions is a solution flow rate of 2.5mL/min for the RC and 3.0mL/min for the SC. **A**. 2mg/L Au and 2mg/L Cd, **B**. 24mg/L Mg, **C**. 0.1mg/L Ag, **D**. 8mg/L Sr, **E**. 1.0mg/L Tl, **F**. 0.1mg/L Na, **G**. 1.0mg/L Li, **H**. 0.5mg/L K, **I**. 0.8mg/L Cs.

**Supplemental Figure 5 (pictures)**



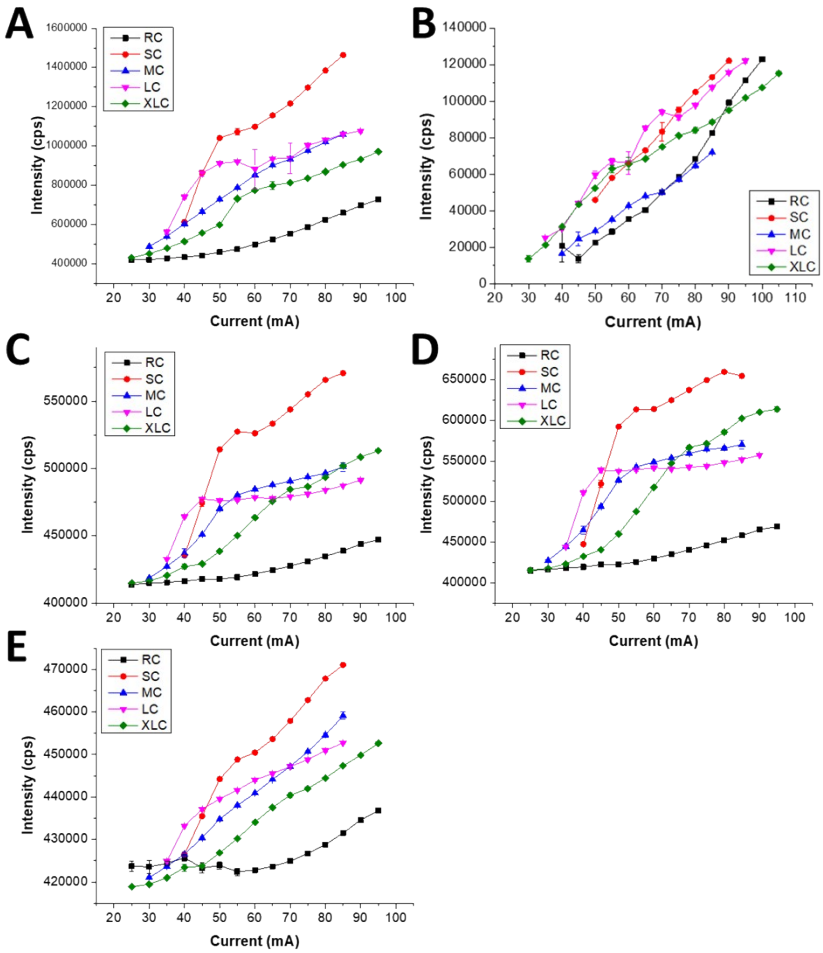

**Supplemental Figure 5:** Pictures of the plasma sampling 0.1M $HNO_3$ at 3.0mL/min with the medium capillary at different applied currents. 3mm discharge gap in each scenario. **A**. 30mA, **B**. 45mA, **C**. 60mA, **D**. 70mA, **E**. 80mA, **F**. 90mA

**Supplemental Figure 6 (videos)**



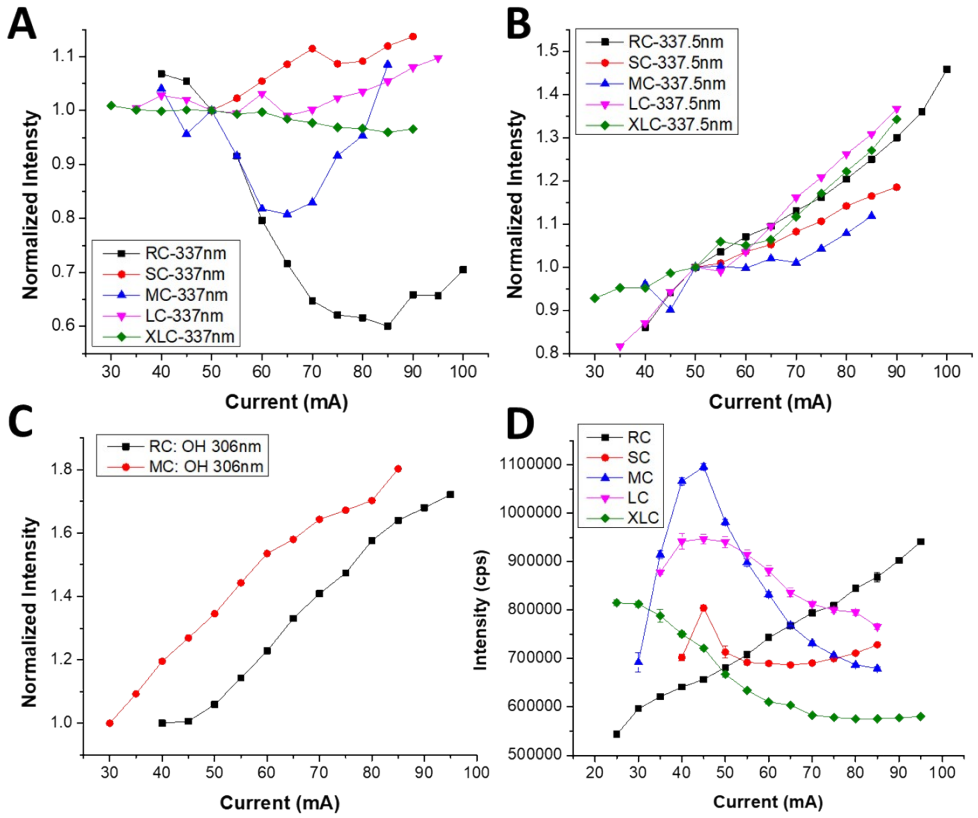

**Supplemental Figure 6:** Videos of the plasma sampling 0.1M $HNO_3$ at 3.0mL/min with the medium capillary at different applied currents. 3mm discharge gap in each scenario. **A**. 35mA, **B**. 70mA, **C**. 80mA, **D**. 80mA with 100mg/L Tl

## Supplemental Figure 7



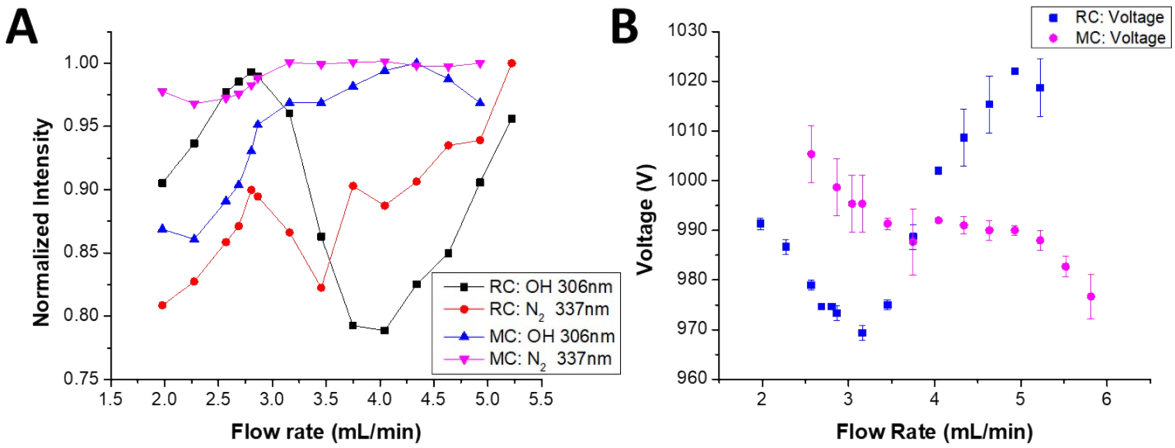

**Supplemental Figure 7:** Effect of applied current on emission. Sample flow for RC: 2.5mL/min. Sample flow for horizontal SCGD capillaries: 3.0mL/min. 3mm discharge gap, 50um slit width, same acquisition settings used throughout. **A**. Cs I 852.1nm (5mg/L). **B**. Ag I 338.2nm (1mg/L). **C**. In I 451.1nm (1mg/L). **D**. Ga I 417.2nm 5mg/L). **E**. Pb I 405.7nm (10mg/L)

**Supplemental Figure 8**




**Supplemental Figure 8:** Effect of applied current on emission. Sample flow for RC: 2.5mL/min. Sample flow for horizontal SCGD capillaries: 3.0mL/min. 3mm discharge gap, 50um slit width, same acquisition settings used throughout. **A**. Emission from nitrogen bandhead at 337nm. **B**. Effect of applied current on the background emission between nitrogen and Ag I 338.2nm. Same parameters as above. **C**. Comparing the effects of current on OH 306nm in the RC and MC. **D**. Emission from H-Alpha, 656.3nm, vs current. 3.0mL/min, 3mm discharge gap, 50um slit width.

**Supplemental Figure 9**




**Supplemental Figure 9:** The effect of increasing flow rate on background emission and voltage when observing the round capillary and medium capillary while sampling 0.1M $HNO_3$. Both studied used a discharge gap of 3mm and 80mA applied current. **A**. OH 306nm and $N_2$ 337nm. **B**. Voltage change vs sample flow rate change.

**Supplemental Figure 10**

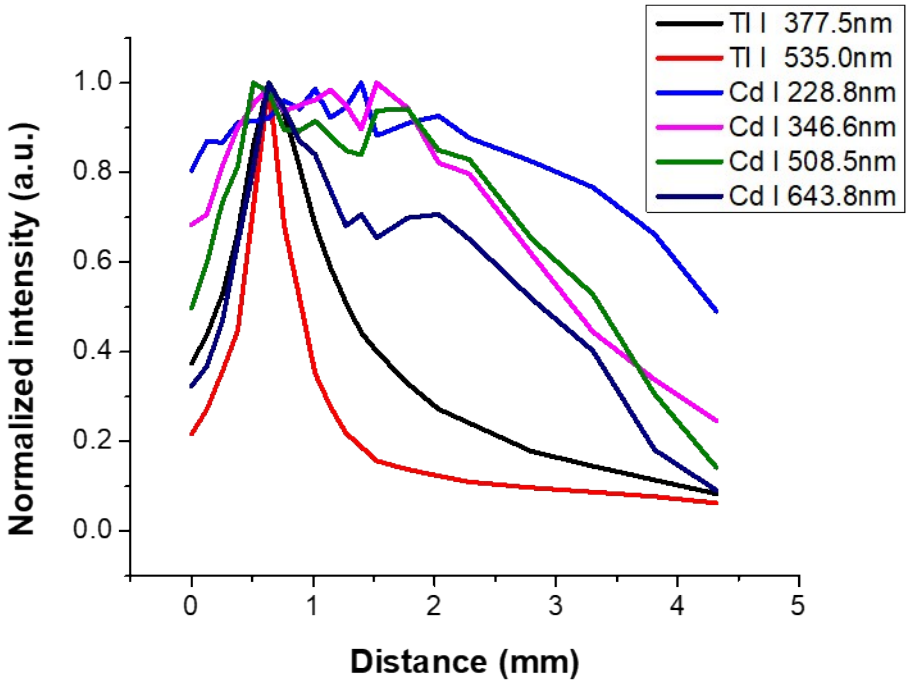
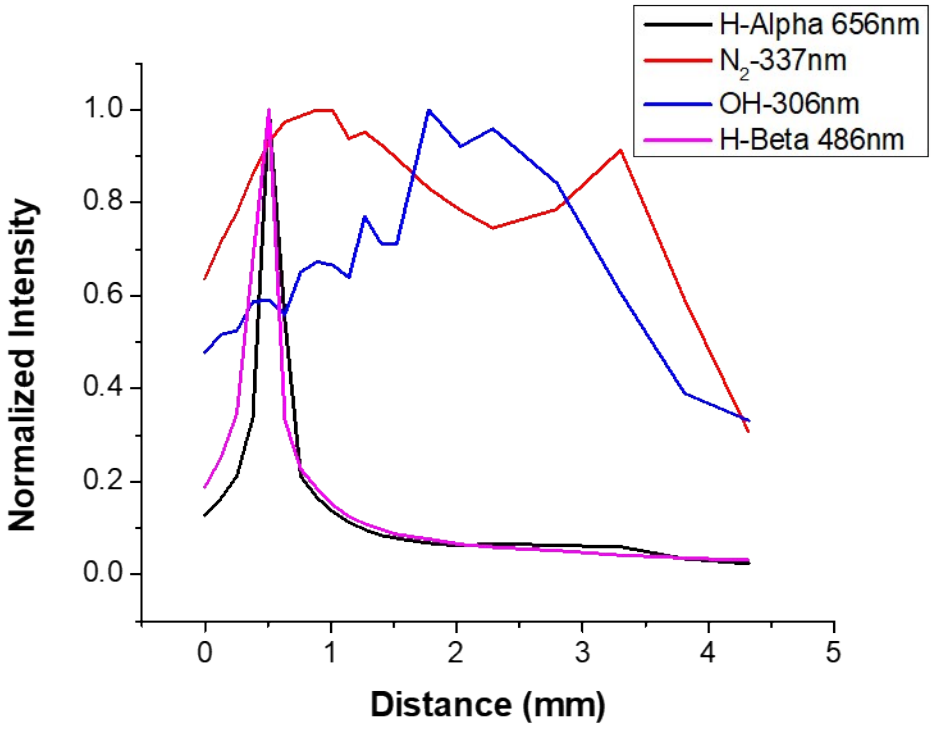


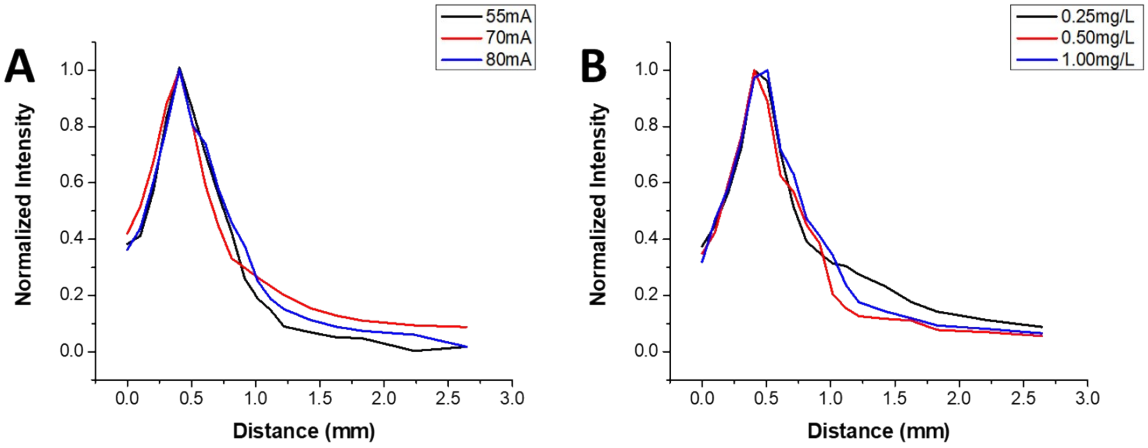

**Figure 10:** Spatial emission profiles for multiple lines of Tl and Cd. Each profile was obtained using a discharge gap of 3mm, an applied current of 80mA, 50µm spectrometer slit, and a flow rate of 3.0mL/min.

**Supplemental Figure 11**



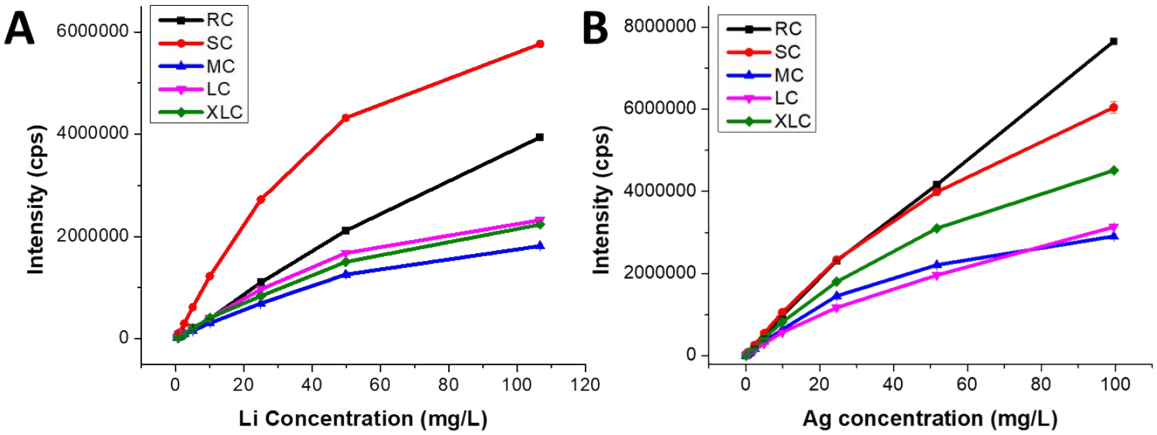

**Supplemental Figure 11:** The spatial emission distribution of selected background species in the SCGD. The medium capillary was used with 80mA applied current, 3.0mL/min sample flow, and a 3mm discharge gap.

**Supplemental Figure 12**



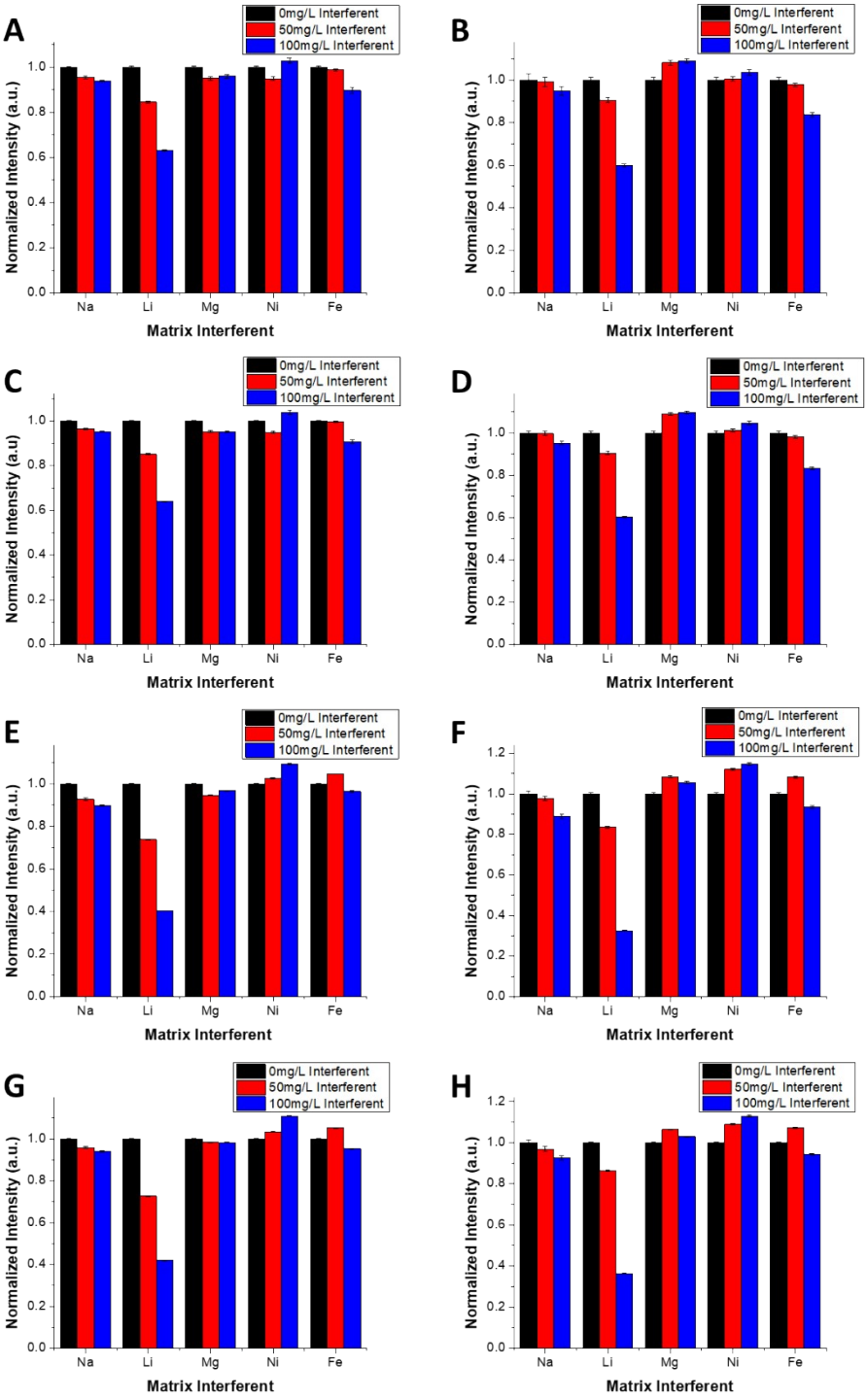

**Supplemental Figure 12:** The spatial variation of In 451.1nm with the medium capillary with 3.0mL/min sample flow, 3mm discharge gap. **A**. Different applied currents **B**. Different concentrations of In.

**Supplemental Figure 13**




**Supplemental Figure 13:** Calibration curves of: **A**) Li I 670.7nm **B**) Ag I 338.2nm, each in 0.1M $HNO_3$ observed with the RC and each horizontal capillary SCGD. Solution flow rates were 2.5mL/min for the RC and 3.0mL/min for each rectangular capillary. In all cases, a 3mm discharge gap, 80mA discharge current.

**Supplemental Figure 14**




**Supplemental Figure 14:** Various matrix interferents and their effect on emission from 1mg/L In and 1mg/L Ga. 3mm discharge gap, 80mA current, 50µm slit. Round capillary: 2.5mL/min sample flow, A: In I 451.1nm, C: In I 410.1nm, E: Ga I 417.2nm, G: Ga I 403.2nm. Medium Capillary: 3.0mL/min, B: In I 451.1nm, D: In I 410.1nm, F: Ga I 417.2nm, H: Ga I 403.2nm.

**Supplemental Table 1**

| | | | RC | | SC | | MC | |
|---|---|---|---|---|---|---|---|---|
| | Element | Wavelength | Slope (cps/mg/L) | LOD (ppb) | Slope (cps/mg/L) | LOD (ppb) | Slope (cps/mg/L) | LOD (ppb) |
| **Narrow** | In | 410.1nm | 9300 | 75 | 95000 | 3.8 | 57900 | 7.6 |
| | | 451.1nm | 14600 | 86 | 155000 | 2.5 | 87900 | 8.4 |
| | Tl | 377.5nm | 42000 | 31 | 76005 | 6.0 | 46900 | 18 |
| | | 535.0nm | 69600 | 6.0 | 176880 | 6.3 | 133000 | 73 |
| | Cs | 852.1nm | 93600 | 130 | 186000 | 7.8 | 134000 | 48 |
| | | 894.3nm | 46300 | 380 | 102000 | 16 | 73200 | 92 |
| | Ga | 403.2nm | 9600 | 43 | 23800 | 15 | 13100 | 41 |
| | | 417.2nm | 19800 | 20 | 51900 | 6.0 | 25900 | 25 |
| | | | | | | | | |
| **Semi-Narrow** | Pb | 368.3nm | 863 | 800 | 4080 | 36 | 2850 | 40 |
| | | 405.7nm | 871 | 1100 | 4380 | 110 | 3450 | 180 |
| | Al | 396.1nm | 614 | 1000 | 745 | 420 | 936 | 220 |
| | Ca | 422.6nm | 5400 | 63 | 3780 | 46 | 2960 | 100 |
| | Na | 588.9nm | 3880000 | 2.6 | 5608000 | 0.4 | 57890000 | 1.7 |
| | | 589.5nm | 2027000 | 5.0 | 2980000 | 0.6 | 2950000 | 2.1 |
| | K | 766.4nm | 1443000 | 30 | 2690000 | 0.9 | 2180000 | 3.2 |
| | | 769.8nm | 764000 | 57 | 1390000 | 0.8 | 1130000 | 6.0 |
| | | | | | | | | |
| **Semi Diffuse** | Ag | 328.0nm | 79000 | 21 | 90600 | 1.1 | 117000 | 2.6 |
| | | 338.2nm | 66500 | 16 | 75200 | 1.0 | 97400 | 1.0 |
| | Pd | 340.4nm | 12700 | 12 | 11500 | 16 | 10100 | 28 |
| | | 360.9nm | 7960 | 21 | 10900 | 21 | 6270 | 63 |
| | Cu | 324.7nm | 24800 | 92 | 61400 | 11 | 42700 | 24 |
| | | 327.3nm | 23800 | 130 | 36300 | 12 | 23600 | 63 |
| | Mg | 285.2nm | 154000 | 8.9 | 279000 | 7.5 | 136000 | 26 |
| | Li | 670.7nm | 723000 | 45 | 1630000 | 5.6 | 868000 | 2.5 |
| | Sr | 460.7nm | 2490 | 430 | 1600 | 190 | 2630 | 260 |
| | Cr | 357.8nm | 604 | 250 | 235 | 460 | 487 | 920 |
| | | 425.4nm | 1130 | 420 | 251 | 740 | 465 | 680 |
| | Ni | 341.4nm | 1920 | 61 | 1440 | 54 | 1910 | 70 |
| | | 352.4nm | 1810 | 1000 | 1920 | 300 | 2630 | 490 |
| | Co | 345.3nm | 1550 | 160 | 1070 | 85 | 918 | 140 |
| | | | | | | | | |
| **Diffuse** | Cd | 228.8nm | 4700 | 110 | 6490 | 8.1 | 4410 | 24 |
| | Zn | 213.8nm | 3860 | 120 | 3360 | 20 | 2070 | 52 |
| | Fe | 248.3nm | 1400 | 370 | 940 | 120 | 854 | 180 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Au | 242.7nm | 2420 | 230 | 1910 | 58 | 1820 | 85 |
| | | 267.5nm | 3570 | 180 | 2840 | 56 | 2660 | 94 |
| | Bi | 223.0nm | 137 | 6000 | 95 | 510 | 77 | 2300 |
| | Mn | 403.0nm | 1200 | 560 | 1650 | 89 | 1420 | 150 |

**Supplemental Table 1:** Full table of backgrounds at the given emission lines and RSDs

**Supplemental Table 2**

| | | | RC | | SC | | MC | |
|---|---|---|---|---|---|---|---|---|
| | Element | Wavelength | Slope (cps/mg/L) | LOD (ppb) | Slope (cps/mg/L) | LOD (ppb) | Slope (cps/mg/L) | LOD (ppb) |
| **Narrow** | In | 410.1nm | 9300 | 75 | 95000 | 3.8 | 57900 | 7.6 |
| | | 451.1nm | 14600 | 86 | 155000 | 2.5 | 87900 | 8.4 |
| | Tl | 377.5nm | 42000 | 31 | 76005 | 6.0 | 46900 | 18 |
| | | 535.0nm | 69600 | 6.0 | 176880 | 6.3 | 133000 | 73 |
| | Cs | 852.1nm | 93600 | 130 | 186000 | 7.8 | 134000 | 48 |
| | | 894.3nm | 46300 | 380 | 102000 | 16 | 73200 | 92 |
| | Ga | 403.2nm | 9600 | 43 | 23800 | 15 | 13100 | 41 |
| | | 417.2nm | 19800 | 20 | 51900 | 6.0 | 25900 | 25 |
| | | | | | | | | |
| **Semi-Narrow** | Pb | 368.3nm | 863 | 800 | 4080 | 36 | 2850 | 40 |
| | | 405.7nm | 871 | 1100 | 4380 | 110 | 3450 | 180 |
| | Al | 396.1nm | 614 | 1000 | 745 | 420 | 936 | 220 |
| | Ca | 422.6nm | 5400 | 63 | 3780 | 46 | 2960 | 100 |
| | Na | 588.9nm | 3880000 | 2.6 | 5608000 | 0.4 | 57890000 | 1.7 |
| | | 589.5nm | 2027000 | 5.0 | 2980000 | 0.6 | 2950000 | 2.1 |
| | K | 766.4nm | 1443000 | 30 | 2690000 | 0.9 | 2180000 | 3.2 |
| | | 769.8nm | 764000 | 57 | 1390000 | 0.8 | 1130000 | 6.0 |
| | | | | | | | | |
| **Semi Diffuse** | Ag | 328.0nm | 79000 | 21 | 90600 | 1.1 | 117000 | 2.6 |
| | | 338.2nm | 66500 | 16 | 75200 | 1.0 | 97400 | 1.0 |
| | Pd | 340.4nm | 12700 | 12 | 11500 | 16 | 10100 | 28 |
| | | 360.9nm | 7960 | 21 | 10900 | 21 | 6270 | 63 |
| | Cu | 324.7nm | 24800 | 92 | 61400 | 11 | 42700 | 24 |
| | | 327.3nm | 23800 | 130 | 36300 | 12 | 23600 | 63 |
| | Mg | 285.2nm | 154000 | 8.9 | 279000 | 7.5 | 136000 | 26 |
| | Li | 670.7nm | 723000 | 45 | 1630000 | 5.6 | 868000 | 2.5 |
| | Sr | 460.7nm | 2490 | 430 | 1600 | 190 | 2630 | 260 |
| | Cr | 357.8nm | 604 | 250 | 235 | 460 | 487 | 920 |
| | | 425.4nm | 1130 | 420 | 251 | 740 | 465 | 680 |
| | Ni | 341.4nm | 1920 | 61 | 1440 | 54 | 1910 | 70 |
| | | 352.4nm | 1810 | 1000 | 1920 | 300 | 2630 | 490 |
| | Co | 345.3nm | 1550 | 160 | 1070 | 85 | 918 | 140 |
| | | | | | | | | |
| **Diffuse** | Cd | 228.8nm | 4700 | 110 | 6490 | 8.1 | 4410 | 24 |
| | Zn | 213.8nm | 3860 | 120 | 3360 | 20 | 2070 | 52 |
| | Fe | 248.3nm | 1400 | 370 | 940 | 120 | 854 | 180 |
| | Au | 242.7nm | 2420 | 230 | 1910 | 58 | 1820 | 85 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 267.5nm | 3570 | 180 | 2840 | 56 | 2660 | 94 |
| | Bi | 223.0nm | 137 | 6000 | 95 | 510 | 77 | 2300 |
| | Mn | 403.0nm | 1200 | 560 | 1650 | 89 | 1420 | 150 |

**Supplemental Table 2:** Full table of calibration curves obtained with the RC, SC, and MC.

**Supplemental Table 3**

| Element and emission line | Limits of Detection (ppb) | | | |
|---|---|---|---|---|
| | RC | MC | SC | SC + PC |
| Cu I 324.7nm | 92 | 24 | 11 | 0.054 |
| Cu I 327.3nm | 127 | 63 | 12 | 0.077 |
| Pb I 368.3nm | 799 | 40 | 36 | 0.72 |
| Pb I 405.7nm | 1065 | 88 | 81 | 0.9 |

**Supplemental Table 3:** Limits of detection obtained for Cu and Pb using continuous flow analysis with capillaries (type: RC, SC, MC) and with preconcentration and the smallest rectangular capillary (type: SC). Discharge current was 80mA, 50µm spectrometer slit and a 3mm discharge gap was used throughout.