Hybrid Capillary/Microfluidic System for Comprehensive Online Liquid Chromatography-Capillary Electrophoresis-Electrospray Ionization-Mass Spectrometry

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Abstract: The supporting information for this manuscript contains additional figures detailing the performance of the hybrid LC-CE-ESI device. A figure comparing peak widths from LC-MS and LC-CE-MS is included to show that the capillary to microchip connection did not cause excessive band broadening. The second figure shows three replicate LC-CE-MS chromato-electropherograms to demonstrate the reproducibility of the method.

## Band broadening from the capillary to microchip transfer

Identical LC runs were performed using a standard capillary spray tip interface and the microchip CE-ESI interface. By displaying a small m/z range and aligning the traces, we can compare the observed peak widths for peptide bands with and without the capillary to microchip transfer. Figure S1 shows that band widths and shapes were very similar for LC-MS and LC-CE-MS indicating that the capillary to microchip connection was not a major source of band broadening.

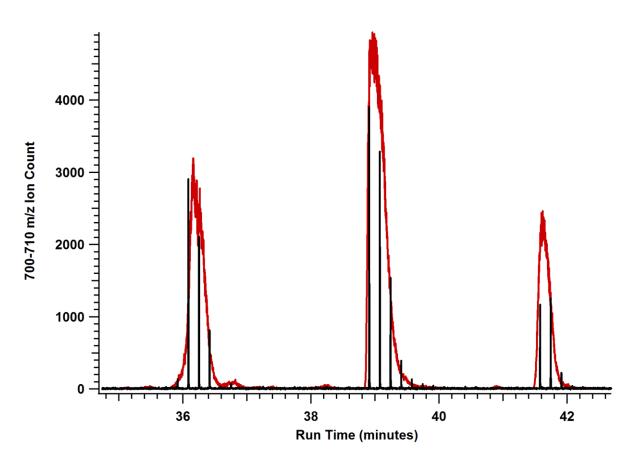


Figure S1. Extracted ion plots for the LC-MS (red) and LC-CE-MS (black) separations of the 5-protein tryptic digest. The LC-MS trace was shifted by +0.45 minutes to better align the peaks; and the LC-CE-MS trace was shifted down by 20 counts to align the baselines.

## Reproducibility of same day replicate LC-CE-MS

Three consecutive LC-CE-MS runs were performed to assess the reproducibility of the method. Multidimensional image plots from these three runs are shown in figure S2. The relative standard deviation for LC retention time and CE migration time were both below 1%.

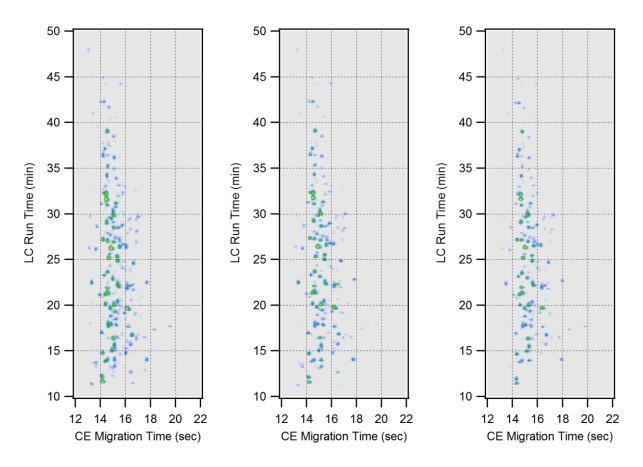


Figure S2. Same day replicate LC-CE-MS separations of the 5 protein tryptic digest. The spot colors indicate base peak ion count.