Electronic Supplementary Material (ESI) for Analyst.

Supporting information for

Solvent Gradient Electrospray for Laser Ablation Electrospray Ionization Mass Spectrometry

Hang Li,[a,b] and Akos Vertes*[a]

[a]*Department of Chemistry, W. M. Keck Institute for Proteomics Technology and Applications, The George Washington University, Washington, DC 20052.*

[b]*National Center for Protein Sciences Beijing, State Key Laboratory of Proteomics, Beijing Proteome Research Center, Beijing Institute of Radiation Medicine, China.*

*Corresponding author. E-mail: vertes@gwu.edu (A. Vertes), Phone: +1 (202) 994-2717, Fax: +1 (202) 994-5873.

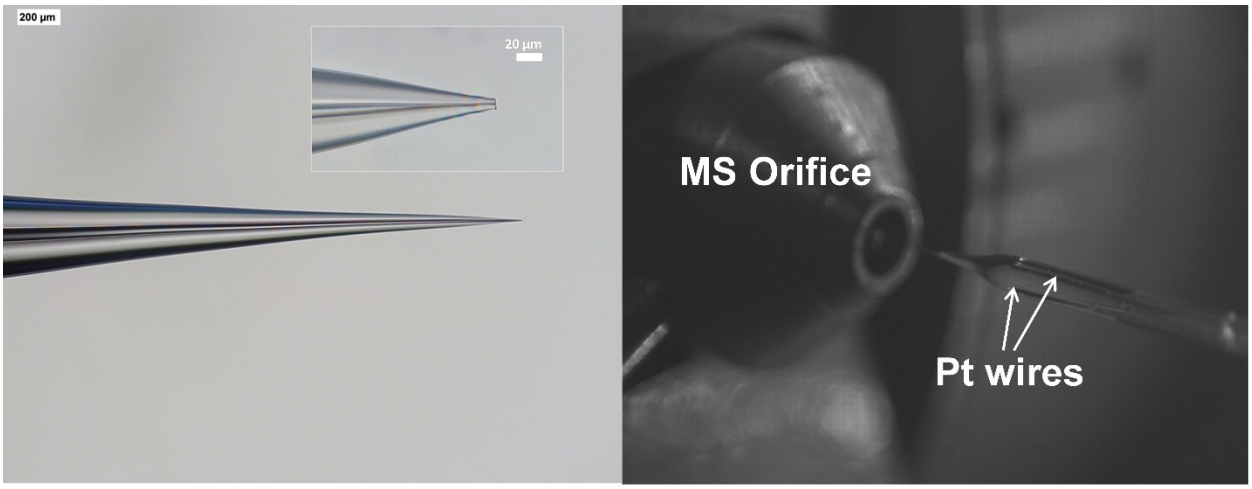

Figure S1. (a) Pulled theta glass capillary with a typical tip diameter of ~3 µm. Image in the inset at higher magnification shows a larger tip diameter of ~8 µm with a ~1 µm wide septum that reaches the tip of the capillary. (b) Pulled theta glass capillary in front of the mass spectrometer inlet orifice with two platinum wire electrodes inserted for generating gradient electrospray.

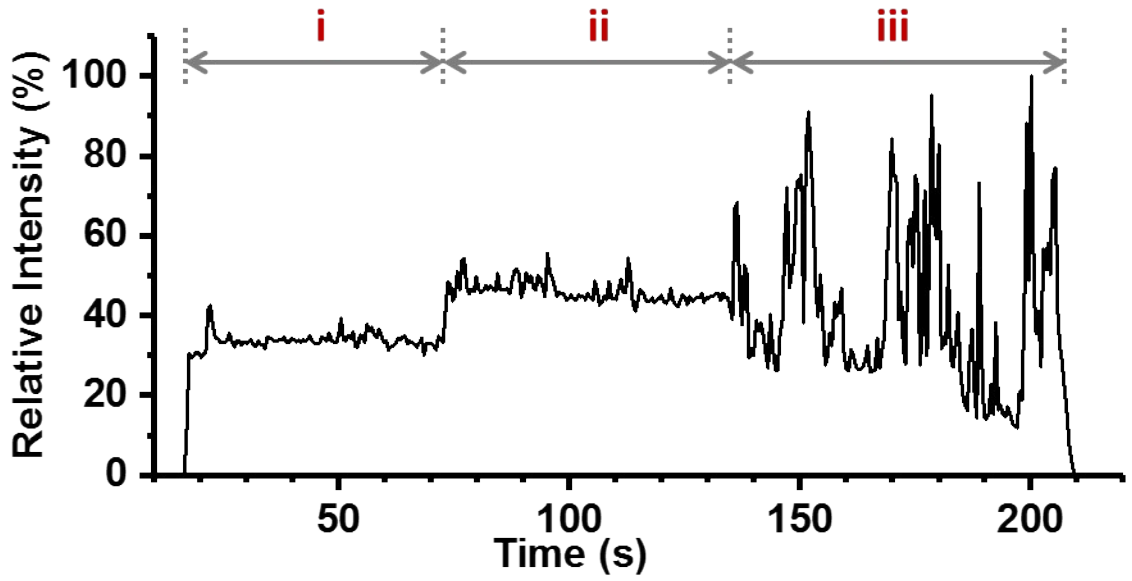

Figure S2. Time dependence of verapamil ion intensity showed a transition from (i) stable signal at 800 V spray voltage, (ii) through slight fluctuations at 1800 V, (iii) to a highly unstable spray at 2800 V.

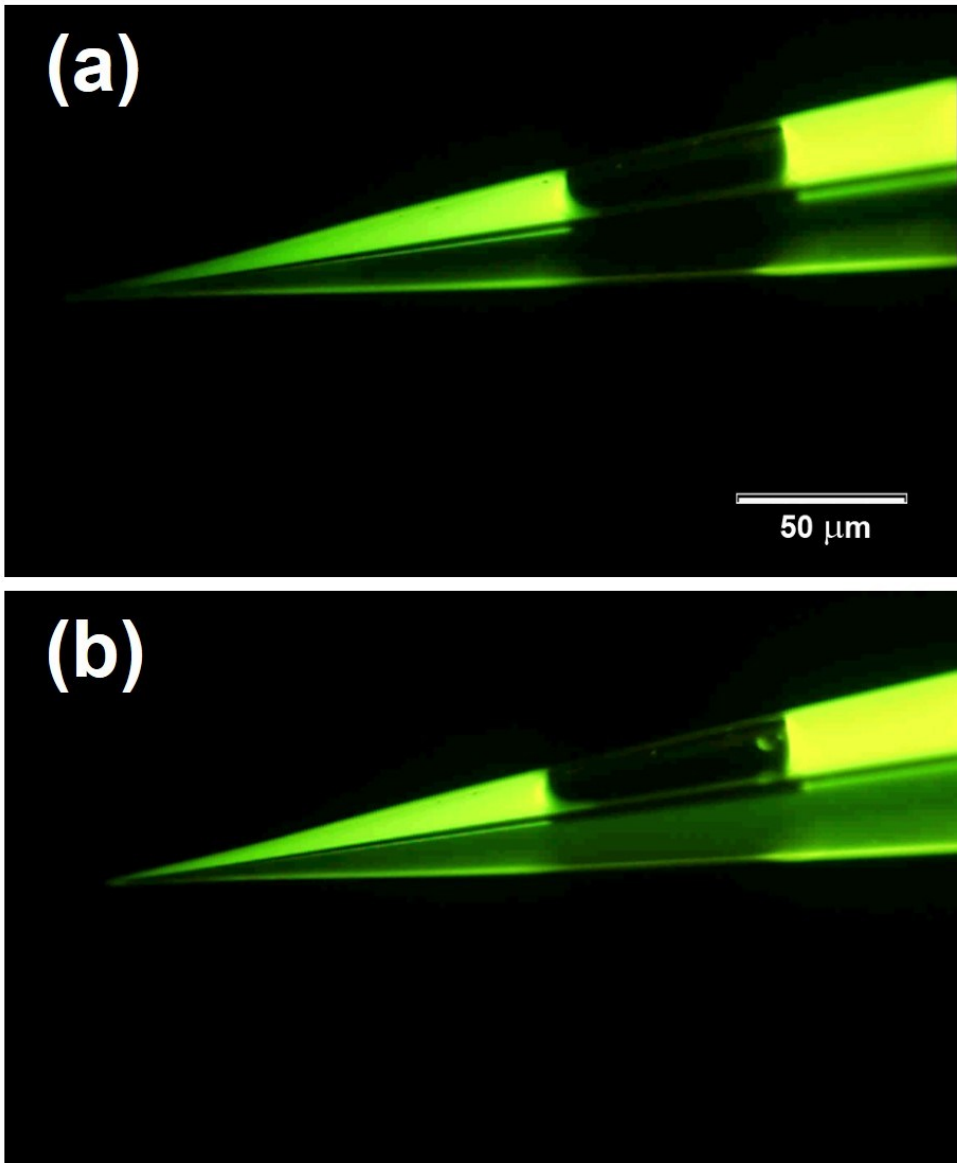

Figure S3. (a) Fluorescence microscope image (excitation at 470-490 nm and emission at 520 nm) of theta capillary of >5 μm tip diameter with barrels loaded with 6 mM rhodamine 6G and water before voltages are applied. (b) Applying 500 V and 300 V to the barrels containing rhodamine 6G solution and water, respectively, results in electroosmosis.

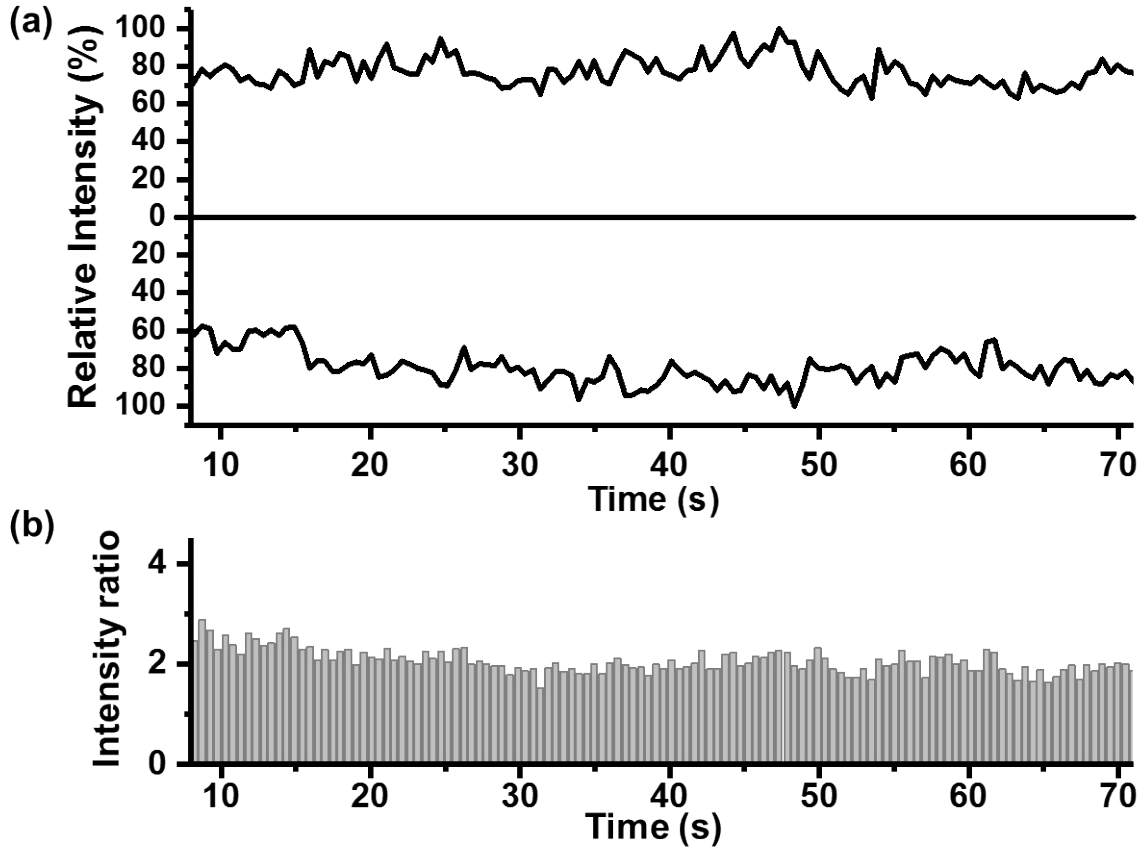

Figure S4. (a) Time dependence of ion intensities from two barrels of a theta capillary. Barrels are loaded with 0.76 μM arginine at 1500 V (spray 1, top trace), and 0.20 μM verapamil at 1000 V (spray 2, bottom trace). (b) Signal intensity ratio of arginine to verapamil (spray 1 to spray 2) as a function of time.