Supplementary Information

Electrothermal Supercharging of Proteins in Native MS: Effects of Protein Isoelectric Point,

Buffer, and nanoESI-Emitter Tip Size

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a)		c)	e)
1000 nm			
o.d.	1683 ± 109	741 ± 134	326 ± 25
i.a. divider	1399 ± 120 175 ± 16	456 ± 37 104 ± 22	198 ± 51 64 ± 6
b)		d)	f)
o.d.	1248 ± 68	572 ± 60	284 ± 7
i.d.	903 ± 113	337 ± 30	105 ± 11

Figure S-1. Electron micrographs of the tips of the theta-glass emitters with average outer diameters of (a,b) 1465 ± 134 , (c,d) 656 ± 131 , and (e,f) 305 ± 32 nm with the inner divider perpendicular to and parallel to the sample stand in the upper and lower panels, respectively.



Figure S-2. Mass spectra of hMb (pI = 7.4) under native MS conditions (700 V spray potential) in aqueous solutions containing 100 mM (a) ammonium acetate (pH = 6.7), (b) ammonium formate (pH = 6.5), and (c) ammonium bicarbonate (pH = 8.3) acquired with ~1465 nm o.d. tips.



Figure S-3. Mass spectra of cyt *c* (pI = 10.3) under native MS conditions (700 V spray potential) in aqueous solutions containing 100 mM (a) ammonium acetate (pH = 6.7), (b) ammonium formate (pH = 6.5), and (c) ammonium bicarbonate (pH = 8.3) acquired with ~1465 nm o.d. tips. Percentages are the relative abundances of the unfolded fractions (\geq 10+ charge states) of cyt *c*.



Figure S-4. Mass spectra of β -lac A (pI = 5.1) under native MS conditions (700 V spray potential) in aqueous solutions containing 100 mM (a) ammonium acetate (pH = 6.7), (b) ammonium formate (pH = 6.5), and (c) ammonium bicarbonate (pH = 8.3) acquired with ~1465 nm o.d. tips. Percentages are the relative abundances of the unfolded fractions (\geq 10+ charge states) of β -lac A.