Development and Characterizations of A Miniature Capillary Electrophoresis Mass Spectrometry System

Supporting Information

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Flow rate.

The flow rate of the nano-ESI spray can be estimated by the consumption solution volume in unit time.[1] The calculation formula is as follows,

$$q_{\mathrm{ESI}} = \frac{\Delta V}{\Delta t} = \frac{\pi r^2 \times \Delta l}{\Delta t} = \frac{\pi d^2 \times \Delta l}{4\,\Delta t} \tag{1}$$

where ΔV is the consumption solution volume in monitoring time, Δl is the consumption solution length in monitoring time, Δt is the monitoring time, r is the radius of the nano-ESI spray capillary, d is the internal diameter of the nano-ESI spray capillary.

Applying a 1.8 KV HV2 for the nano-ESI spray with 11.26 μm tip, the consumption solution length in one hour is 7 mm. The internal diameter of the nano-ESI spray capillary is 0.86 mm, and the flow rate can be calculated as follows,

$$q_{\mathrm{ESI}} = \frac{\pi d^2 \times \Delta l}{4\,\Delta t} = \frac{3.14 \times (0.86\mathrm{mm})^2 \times 7\mathrm{mm}}{4 \times 60\mathrm{min}} \times 10^3 = 67.75\,\mathrm{nL/min} \tag{2}$$

The flow rate within the CE capillary was estimated by the electroosmotic velocity, and the calculation formula can be written as,

$$q_{\mathrm{CE}} = v\, s_{\mathrm{CE}} = v\frac{\pi d^2}{4} \tag{3}$$

where v is the electroosmotic velocity, s_{CE} is the cross-sectional area of separation capillary, d is the internal diameter of the CE separation capillary.

Applying a 7 KV separation voltage for the CE capillary (20 cm×50 μm i.d.) , the solution migrated via the whole capillary need 6 minutes. The flow rate can be calculated as follows,

$$q_{\mathrm{CE}} = v\frac{\pi d^2}{4} = \frac{200\ \mathrm{mm}}{6\ \mathrm{min}} \times \frac{3.14 \times (50\ \mu\mathrm{m})^2}{4} \times 10^{-3} = 65.41\,\mathrm{nL/min} \tag{4}$$

CE peak narrowing effect in Figure 2b.

Possible reasons about the peak broadening was that: the diffusion of analytes in the spray emitter would broaden the sample plug, however, the diluted analyte concentration and low MS sensitivity would narrow the detected peak as shown in the following figure. In the case in Figure 2b, the narrowing effects might be dominant, thus results in a narrower peak when L = 1.5 mm.

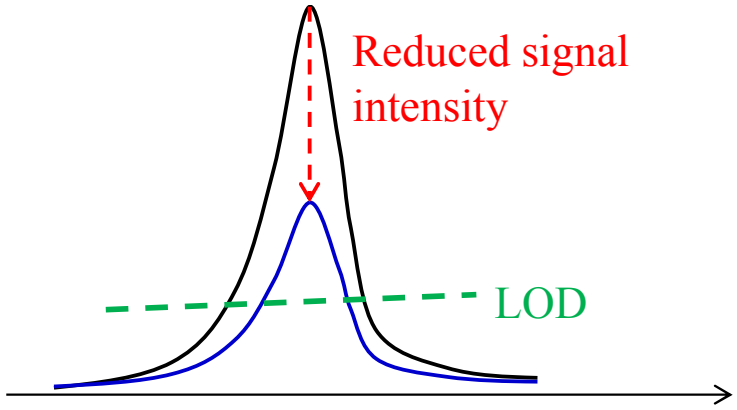

Figure S1. Schematic representation of the peak narrowing effects due to the analyte dilution and limited LOD of the mini MS.

Detection limit.

Limit of detection (LOD) of the CE/MS system was characterized for rhodamine B and MRFA as shown in Figure S2. The experimental conditions are summarized in the main text. For rohdamine B, the LOD is 1 μg/mL, and a LOD of 5 μg/mL is obtained for MRFA (the signal-noise-ratio at LOD is ~3:1).

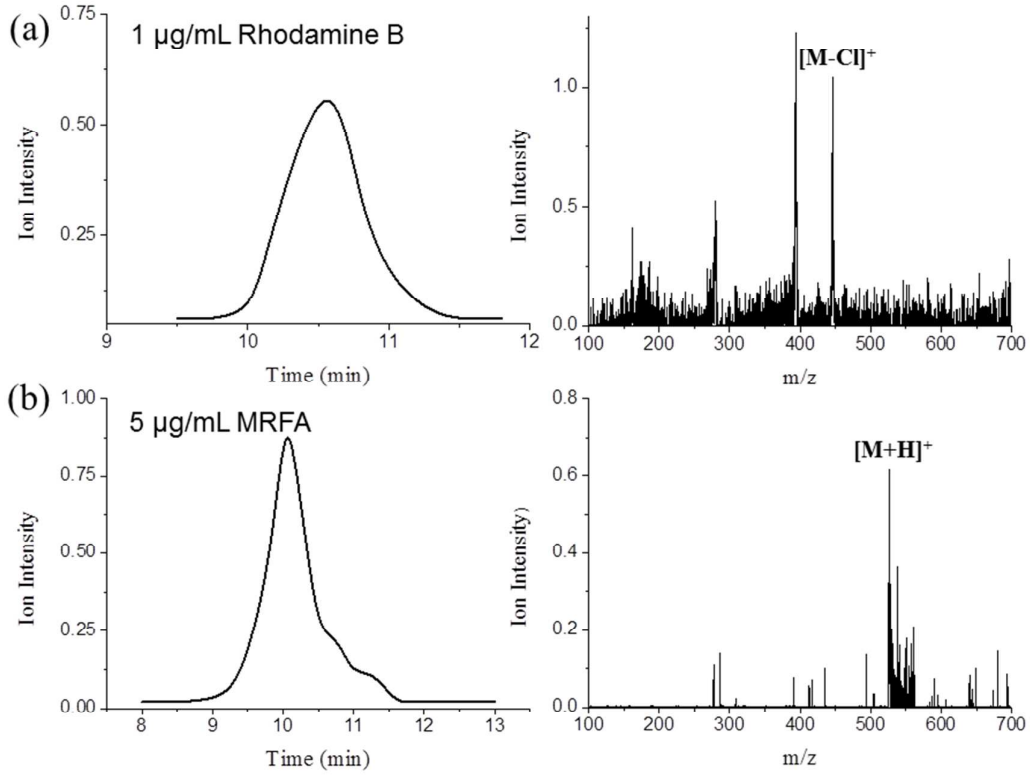

Figure S2. CE/MS limit of detection. (a) 1 μg/mL rhodamine B electropherogram (left) and mass spectrum (right). (b) 5 μg/mL MRFA electropherogram (left) and mass spectrum (right).

CE separation voltage.

CE separation voltage effects were studied, and the results were plotted in Figure S3 with CE separation voltages of 15 kV, 10 kV and 5 kV, respectively. A mixture sample of three peptides was separated. From left to right, the peaks are bradykinin, angiotensin I and angiotensin II. With a higher separation voltage, the sample has a narrower peak but lower separation resolution. A Lower separation voltage is advantageous in terms of improving the separation resolution, but result in peak

broadening. Considering limitations of the system, a 7 KV separation voltage was applied in the following experiments.

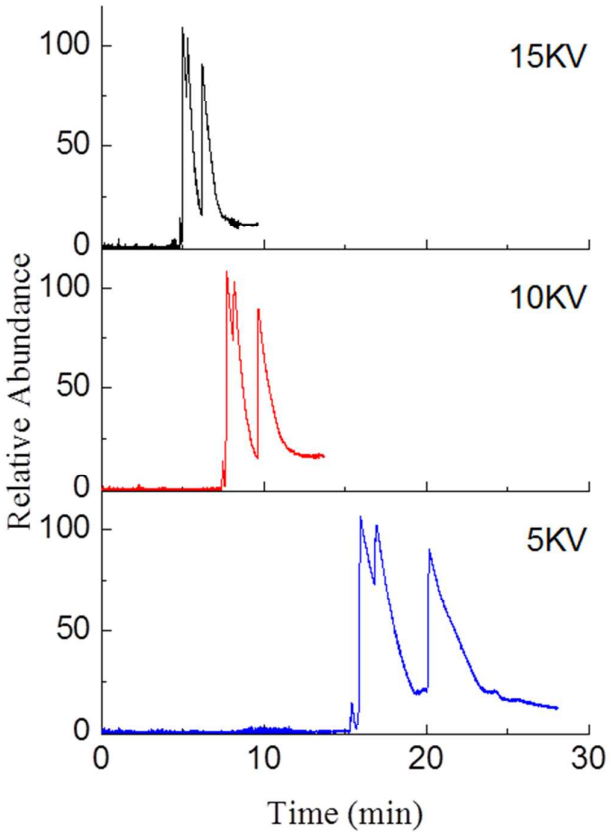

Figure S3. CE separation voltage effects. From left to right, the peaks are bradykinin (2 mg/mL), angiotensin I (4 mg/mL) and angiotensin II (2 mg/mL). Capillary length 40 cm.

Reference

1. W. Xu, N. Charipar, M. A. Kirleis, Y. Xia, Z. Ouyang, *Analytical Chemistry* 2010, *82*. 6584-6592, DOI: 10.1021/ac101002t.