Electronic Supplementary Material (ESI) for Lab on a Chip


# Label-free quantitation of peptide release from neurons in a microfluidic device with mass spectrometry imaging

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**Supplementary Information**

## Details of the adsorption model

For the results shown in Fig. 2, we made several simplifying assumptions. We assumed that each adsorbate molecule (A, B, and C) occupy the same area of 1 nm × 1 nm, and differ only by adsorption rate constants. The number of analyte binding sites per segment (200 μm × 200 μm) is therefore $4 \times 10^{10}$ with 500 segments along the 10 cm-long channel. The size may be varied depending on the analytes of interest.

Consider adsorption of two analytes A and B. When two analytes adsorb onto the substrate, the adsorption is competitive between the two.

$$A + \theta \xrightarrow{k_A} A\theta$$

$$B + \theta \xrightarrow{k_B} B\theta$$

Using the site and material balance:

$$[\theta]_T = [\theta] + [A\theta] + [B\theta]$$

$$[A]_O = [A] + [A\theta],\ [B]_O = [B] + [B\theta]$$

the adsorption rate can be described:

$$\frac{d[A\theta]}{dt} = k_A[A][\theta] = k_A([A]_O - [A\theta])([\theta]_T - [A\theta] - [B\theta])$$

$$\frac{d[B\theta]}{dt} = k_B[B][\theta] = k_B([B]_O - [B\theta])([\theta]_T - [A\theta] - [B\theta])$$

The coupled differential equations can be solved for an initially clean surface ( [Aθ] = [Bθ] = 0 at t = 0), and the solutions are plotted in Fig. 2F. We used the *ode15s* function in MATLAB

(MathWorks, version 7.12, R2011a) to solve the coupled ordinary differential equations. $[A]_o$ and $[B]_o$ in each segment are determined based on the amount of A and B consumed by the previous segment.

The adsorption kinetics of three analytes (A, B, and C) were obtained in a similar manner by solving three coupled differential equations. The parameters used in Fig. 2G are $k_A = 10k_B = 100k_C = 100000\ M^{-1}s^{-1}$ and v = 0.83 mm/s.

## Influence of concentration and flow rate on length measurement

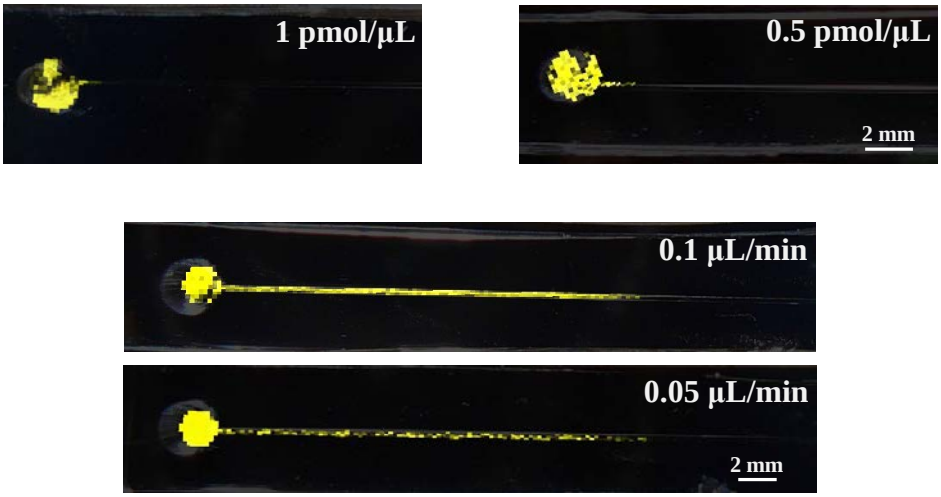


**Figure S1.** MS images of AP with different concentrations and flow rates. A microfluidic device with a straight channel (200 µm width × 50 µm height × 30 mm length) was used here instead, but the experimental procedure was the same as the standard peptide experiments on the serpentine channel. The concentrations of 1 and 0.5 pmol/µL were compared on 3 pmol AP, and the flow rates of 0.1 and 0.05 µL/min were compared on 4 pmol AP. Yellow color indicates the presence of AP. In both cases, the measured length remains almost constant and is insensitive to the changing parameter.