Electronic Supplementary Material (ESI) for Lab on a Chip.

Supporting Information

Delayed voltammetric with respect to amperometric electrochemical detection of concentration changes in microchannels

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In this file of Supporting Information, we provide additional details on

- **the processing routine for the CV data;**
- **the method used to assess the electrode capacitance from CV background traces;**
- **The numerical values for σ_{AMP} and σ_{CV} (Table S1);**
- **a method to estimate the relaxation time of the diffusion layer through an analogy with electronics;**
- **the direct acquisition of the MTF from sine concentration waves (Figure S3).**

Obtaining the peak current i_p from raw CV data

The raw CV data obtained during the experiments featured two characteristics, which could potentially complicate the data analysis. First, because of the relatively high scan rate (10 V s^{-1}) used for these experiments, the background current was quite important and could potentially hinder the determination of the concentration profiles from the voltammetric data. Additionally, minute variations in the first voltage sweeps of the acquisition, due to electrode discharge or stabilization, could introduce further inaccuracies.

For these reasons, CV measurements were performed in the background buffer (PBS) and were substracted from the raw data (Figure S1). This background substraction method is routinely used for the processing of fast-scan CV data. From the resulting signal, the peak currents i_p could be identified, and the time variations of these currents was analyzed and plotted on graphs, such as the ones presented in the main text.

Calculating the electrode capacitance

An electrode capacitance can be typically defined by considering the time dependent transport of a charge Q and the potential difference ΔE over the electrode, following

$$Q(t) = C\ \Delta E(t) \qquad \text{(S1)}$$

The time derivative of this equation leads to

$$\frac{\partial}{\partial t} Q(t) = i(t) = \frac{\partial}{\partial t}(C\ \Delta E)(t) = C\ SR \qquad \text{(S2)}$$

where i is the measured current and SR is the scan rate.

It is then possible to estimate the capacitance involved in charging the double layer, C_{dl}, from the double layer current i_c, defined by the hysteresis observed during CV scans performed in background buffer with

$$C_{dl} = \frac{i_c}{2\ SR} \qquad \text{(S3)}$$

From Figure S1 (panel 'CV background'), i_c~60 nA for SR= 10 V s-1. Hence, C_{dl}~3 nF.

Numerical values for σ_{AMP} and σ_{CV}

Table S1: *Variations of the fitting parameters σ_{AMP} and σ_{CV} with the flow rate v.*[a]

v/ µl s^{-1}	N_{AMP}	σ_{AMP}/ s	N_{CV}	σ_{CV}/ s
0.5	4	1.66±0.17	5	1.80±0.03
1	5	1.12±0.05	5	1.47±0.09***
5	5	0.67±0.01	5	0.81±0.05***
10	7	0.25±0.04	8	0.40±0.06***

[a]. The data presented here is the average of N_{AMP} or N_{CV} traces, ± SD. The AMP and CV datasets were compared with a double-tailed Student's t-test, assuming equal variance, ***: $p < 0.001$

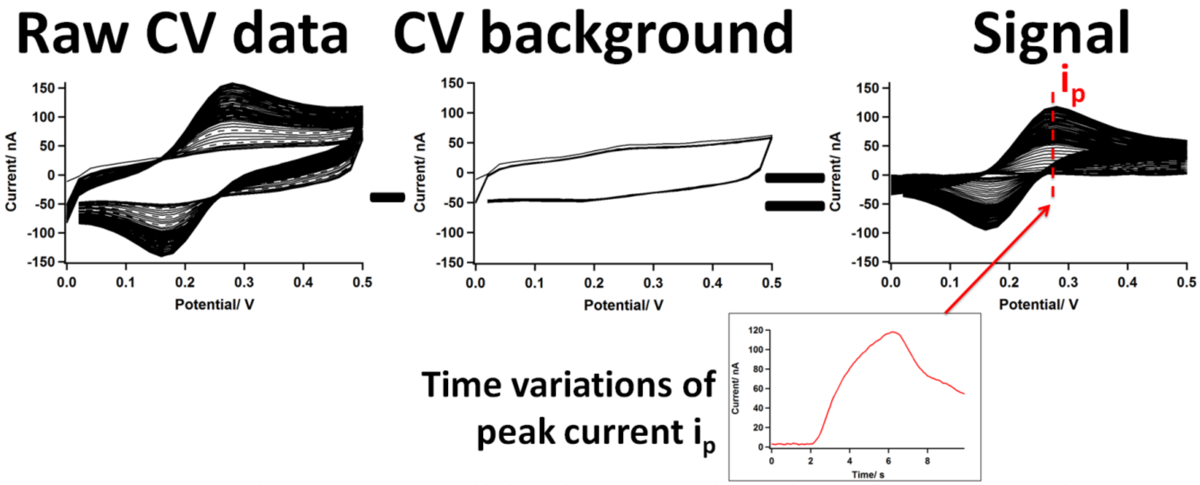

Figure S1: *Data processing routine, showing the background being substracted from the raw data, leading to the final CV signal. The peak currents ip are then plotted as a function of time.*

Calculating the capacitance and delay time τ_D due to the presence of the diffusion layer

Here, an analogy with electronics is used. A linear gradient across a diffusion layer (thickness δ_D) at the surface of an electrode (where the concentration is 0) is considered, as shown on Figure S2. The bulk concentration is C_0.

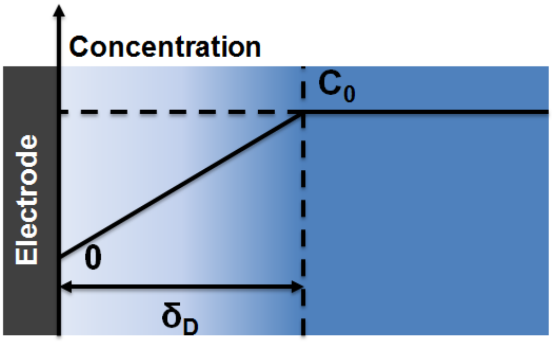

Figure S2: *Scheme of the diffusion layer.*

The diffusive current i_D to the electrode (i.e. the flux of analyte across the electrode surface) is obtained from Fick's first law:

$$i_D = A\,D\,\left\|\overrightarrow{grad}(C)\right\| = \frac{A\,D\,C_0}{\delta_D} \qquad \text{(S4)}$$

where D is the diffusion coefficient, C is the concentration and A is the electrode surface area. This equation describes a flux obtained from a difference of potential energies, and formally shows similarity to Ohm's law. In this case, i_D corresponds to the current, and the concentration C_0 to the potential. Hence, we can define a "diffusive resistance"[1] R_D

$$R_D = \frac{\delta_D}{A\,D} \qquad \text{(S5)}$$

As stated in the previous section, an expression for a diffusive capacitance C_D can be obtained from Eq.S1. The concentration still plays the role of the potential, and the charge is here the number of analyte molecules in the diffusion layer. Following the system geometry presented on Fig.S2

$$C_D = \frac{\frac{AC_0\delta_D}{2}}{C_0} = \frac{A\delta_D}{2} \qquad \text{(S6)}$$

Hence, a characteristic time can be defined for this diffusive RC system with

$$\tau_D = R_D C_D = \frac{{\delta_D}^2}{2D} \qquad \text{(S7)}$$

For a flow rate of 10 µl s^{-1}, we found τ_D= 8 ms (see main text). As D= 7.6 10^{-10} m^2 s^{-1},[2] for these experimental conditions δ_D= 3.5 µm. As a consequence, knowing the size of the electrode (100 µm height, 51 µm diameter) we can evaluate R_D and C_D, leading to R_D= 2.9 10^{11} s m^{-3} and C_D= 2.8 10^{-14} m^3.

Direct acquisition of the MTF

As detailed in the main text, the MTF could be computed directly from sine concentration waves, and by considering the modulation of the contrast (Figure S3).

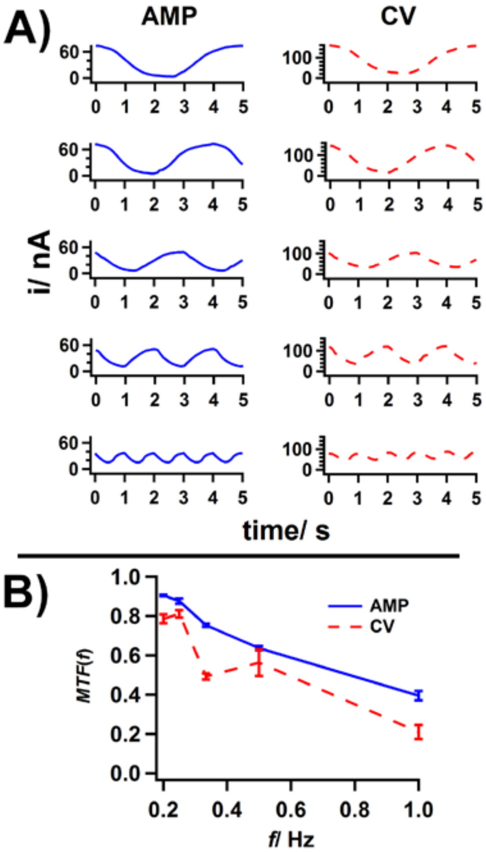

Figure S3: *Experimental analysis of the MTF, obtained by applying sinusoidal concentration variations in the microfluidic chip for a 5 µl s^{-1} flow rate. A) AMP (left) and CV (right) responses to the sinusoidal concentration profile (1 mM for the maximum concentration) with periods decreasing from 5 s to 1 s (top to bottom). B) MTF obtained from these traces, using Eq.14 for AMP (solid line) and CV (dashed line), average ± SD. At least 6 cycles were used to calculate the average, and the MTF computed for AMP was significantly (p < 0.001) higher for all the considered periods.*

References

(1) Mellander, L. J.; Trouillon, R.; Svensson, M. I.; Ewing, A. G. *Sci. Rep.* **2012**, *2*, 907.

(2) Amatore, C.; Da Mota, N.; Lemmer, C.; Pebay, C.; Sella, C.; Thouin, L. *Anal. Chem.* **2008**, *80*, 9483–9490.