Electronic Supplementary Information

In-flow electrochemical detection of chemicals in droplets with pyrolysed photoresist electrodes: application as a module for quantification of microsampled dopamine

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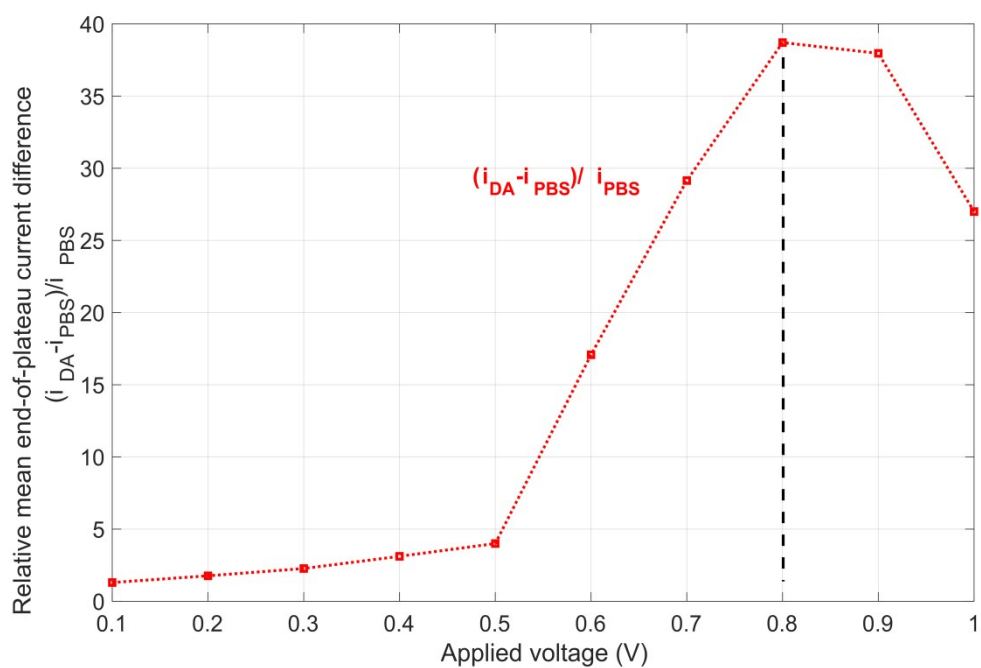# Figure S1 - Voltage sweep experiment

Figure S1 Voltage sweep for the determination of the voltage to apply between working and reference electrodes in order to perform chronoamperometry of DA in droplets of PBS. For each voltage between 0.1V and 1V, between 16 and 31 chronoamperometric signals of droplets were recorded to calculate the mean of the corresponding end-of-plateau values respectively in PBS and DA droplets. The relative deviation of the mean value for DA compared to the one for PBS resulted to a maximum at 0.8V.

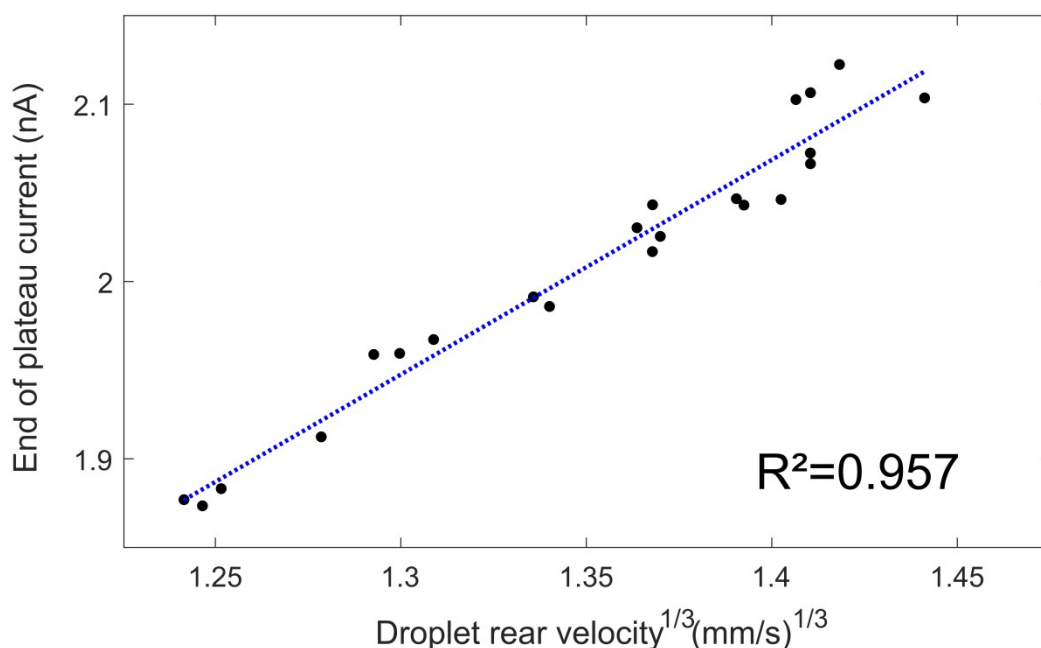# Figure S2 - Velocity-dependence of the end of plateau current

Figure S2 Verification of the Levich law by plotting the end-of-plateau currents of the droplets of 1mM ferrocenemethanol in PBS versus the cubic root of their rear velocity. Measured end-of-plateau currents and linear regression are respectively represented by black dots and blue dotted line.

Considering the 100x16µm2 cross-section of the channels, the velocities 1.25^3 mm/s, 1.35^3 mm/s and 1.45^3 mm/s represent 188nL/min, 236nL/min and 293nL/min respectively. Given the use of a syringe pump, instantaneous flow variations in this range are not surprising. 188nL/min and 293nL/min give 1.88nA and 2.13nA respectively. Considering 236nL/min as the mean flow rate giving 2.01nA, the relative variations of signal are -6.5% and +6.0% respectively. These relative variations are still reasonable and these flows are in the range for microdialysis. If much different flow rates were used, simple methods could be implemented to compensate them: flow rate measurement, correction for velocity dependence according to the Levich law, change of PDMS channel section…

Table S1 - Reporting of the values of Figure 3

[DA] (µM)	Segmented flow			Continuous flow	
	Mean EOPC (pA)	STD (pA)	Ndroplets	Mean LC (pA)	STD (pA)
0	19.244	0.674	43	27.070	0.465
0.05	19.625	0.546	36	23.242	0.951
0.1	18.865	0.461	51	26.488	0.507
0.25	21.946	0.652	48	28.979	0.679
0.5	26.806	0.883	27	37.216	0.646
0.75	27.350	0.963	55	59.817	0.613
1	28.116	2.985	36	61.597	1.369
5	83.276	1.417	60	227.637	1.238
20	259.590	4.620	42	812.570	3.967

EOPC: End-of-plateau current; LC: Limiting current; STD: Standard Deviation; Ndroplets: number of droplets analyzed for the presented data

Table S1 Reporting of the mean current values and standard deviations calculated from experimental measurements in order to draw calibration curves on figure 3