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On-chip label-free protein analysis with downstream electrodes for direct removal of electrolysis products

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Estimation of the electrical resistances of the electrodes and the electrophoresis area

The total electrical resistance of the device comprises of the electrical resistance of the electrophoresis channel $R_{electrophoresis}$, the electrolyte channel $R_{electrolyte}$ and the perpendicular connecting channels $R_{ConnectingChannels}$ linking the electrolyte channel to the electrophoresis area. The resistance of the wider section of the electrolyte channel can be ignored due to its much wider width (1 mm) and hence larger cross-sectional area compared to than that of the narrow section downstream of the connecting channels (width of 100 μ m). The total resistance of the microfluidic device is thus

$$R_{total} = 2 \times (R_{electrolyte} + R_{ConnectingChannels}) + R_{electrophoresis} \quad (1)$$

The resistances of each of the individual components can be estimated from

$$R_i = \frac{1}{\kappa_{3M,KCl}} \frac{L_i}{w_i \times h_i}$$

where L_i , w_i and h_i are the length, width and height of channel *i* and κ_i is the conductivity of the solution flowing in that channel.

To estimate the electrical resistance of the electrodes a highly con-

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ductive solution was flown in the electrophoresis area instead of the sample and the flanking buffer (Figure 1A, Main Text). With equally conductive solution filling all the channels of the device, the resistance of the central electrophoresis channel can be ignored due to its large cross-sectional area and short length (Table 1, Supplementary Materials).

$$R_{electrodes} = 2 \times (R_{electrolyte} + R_{ConnectingChannels}) + R_{electrophoresis,3M}$$

$$z 2 \times (R_{electrolyte} + R_{ConnectingChannels})$$
(2)

Using the values in Table 1 (Supplementray Materials) the total resistance of the device and the electrodes $R_{electrodes}$ can now be estimated to be R_{total} =318 $k\Omega$ and $R_{electrodes}$ =200 $k\Omega$, respectively. These values are in good agreement with the experimentally obtained values (Figure 3A,B).

Estimation of the optimal performance conditions and the resultant analyte beam broadening

To estimate the operating conditions at which the relative width of the beam in the electrophoresis chamber remains minimal, we used equation (1) (Main Text) to minimise the quantity $\frac{\sigma_{total}}{w}$:

$$\left(\frac{\sigma_{total}}{w}\right)^2 = \left(\frac{w_{inj}^2}{12w^2}\right) + \frac{2DL}{vw^2} + \frac{h^2 d^2 v}{105DLw^2}$$

$$= \left(\frac{w_{inj}^2}{12w^2}\right) + 2D\left(\frac{h}{w}\right)\left(\frac{L}{Q}\right) + \frac{C^2}{105D}\left(\frac{Q}{L}\right)\left(\frac{h}{w}\right)$$
(3)

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Table 1 The lengths and cross-sectional areas of the various components that the microfluidic device is composed of together with the conductivities of the solutions flowing in them.

	Electrophoresis channel	Connecting channel	Electrolyte outlet
Solution	10 mM phosphate buffer	3M KCl	3M KCl
Conductivity (S m-1)	0.048	25	25
Length (µm)	1700*	6000	10000
Width (µm)	6000	20	100
Height (µm)	25	25	25
Resistance $(k\Omega)$	118	53	89

* Only this fraction of the electrophoresis chamber was used that the electrolyte ions do not reach. The area where the electrolyte ions diffuse is significantly more conductive than the area where they do not.

where we used the carrier fluid velocity of $v = \frac{O}{wh}$ and deflection of $d = C \times w$ where *C* stands for the relative deflection, i.e. for the fraction of the total width by which the analyte beam has deflected away from its original position. Condition (4) is satisfied when $\frac{Q}{L} = \frac{\sqrt{210} D}{C}$.

Now the minimum possible analyte beam braodening at a specific relative deflection can be described as

From equation (3) it can be concluded that minimum broadening occurs when $\frac{w_{inj}}{w}$ and $\frac{h}{w}$ are minimised and further when

$$\frac{d}{d(\frac{L}{Q})} \left[\left(\frac{\sigma_{total}}{w} \right)^2 \right] = 2D \left(\frac{h}{w} \right) - \frac{C^2}{105D} \left(\frac{Q}{L} \right)^2 \left(\frac{h}{w} \right) = 0$$
(4)

$$\left(\frac{\sigma_{total}}{w}\right)^2 = \left(\frac{w_{inj}^2}{12w^2}\right) + \frac{2C}{\sqrt{210}}\left(\frac{h}{w}\right) + \frac{C\sqrt{210}}{105}\left(\frac{h}{w}\right)$$
$$= \left(\frac{w_{inj}^2}{12w^2}\right) + 2C\sqrt{\frac{2}{105}}\left(\frac{h}{w}\right)$$
(5)