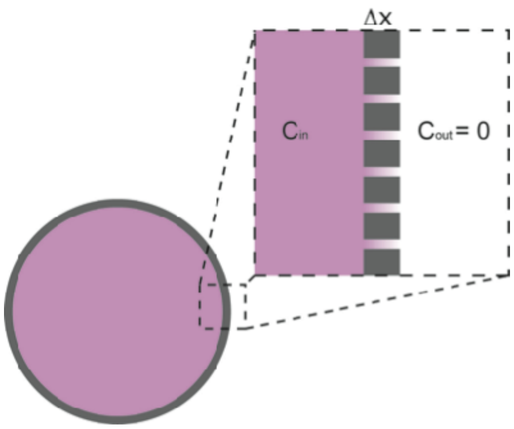
Supplementary Material (ESI) for Lab on a Chip

Supplementary Material: A Lumped Capacitance Model for Predicting Transient Changes in Concentration Within a Nanoporous Reaction Vessel Under Moderate External Flow

We make the following assumptions in our analysis:

1) The internal concentration of the reaction vessel is uniform and well mixed. Based on observations of reaction vessels filled with fluorescent species that leaks out over time this seems a reasonable assumption.
2) Under moderate flow (microliters/hour) there is no appreciable convective transport into or out of the reaction vessel, but the external concentration (C_{out}) of the species leaking from the vessel is effectively zero.
3) For the sake of discretization and simplification the change in concentration across the nanoporous membrane of width Δx is assumed to be linear.



Using Fick's law, the rate of mass (*m*) loss from the reaction vessel can be expressed as follows;

(i) $$\frac{dm}{dt} = -DnM_w A_{pore} \frac{dC}{dx}$$

A_{pore} is the cross sectional area of a single pore and is the product of the pore height and width ($h_p w_p$), *n* is the number of pores, *D* is the diffusivity of the species of interest and *C* is concentration. Discretizing this expression based on the assumptions enumerated above for a short time increment *Dt,* the change in concentration can be expressed as;

(ii) $$\Delta C = \frac{-Dnh_p w_p}{V\Delta x}(C_{in} - C_{out})\Delta t$$

where *Dx* is the membrane thickness, and *V* is the total volume of the reaction vessel. Using (ii), and noting that the concentration outside of the vessel is always zero, the following expression can be written for the concentration within the vessel at *t*+*Dt*.

(iii) $$C_{in}^{t+\Delta t} = C_{in}^{t} - \frac{Dnh_p w_p}{V\Delta x} C_{in}^{t}\Delta t$$

or

$$C_{in}^{t+\Delta t} = C_{in}^{t}\left(1 - \frac{Dnh_p w_p \Delta t}{V\Delta x}\right)$$

Thus the concentration within the vessel for an arbitrary time t+kDt can be given as;

(iv) $$C_{in}^{t+k\Delta t} = C_{in}^{t}\left(1 - \frac{Dnh_p w_p \Delta t}{V\Delta x}\right)^k$$

Equation (iv) was used to calculate the predicted normalized concentration within porous reaction vessels over a 30 minute period. The vessel dimensions were 15µm high, 40µm diameter, 2μm membrane thickness. The 56 slit-shaped pores were estimated to be 10μm deep. Graphs of concentration over time were calculated using a time step of 0.01 seconds and pore sizes of 200nm and 20nm for a range of diffusivities representing expected diffusivities for molecular species from a few hundred to tens of nanometers in diameter.