Supporting Information

Numerical modeling of solid phase microextraction: binding matrix effect on equilibrium time

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Boundary conditions at the coating/solution interface

At the coating/solution boundary, the conditions that ensure continuity of the dependent variables in the fiber coating and aqueous solution were specified. This specification is needed due to the nature of the analyte concentrations found at these two sites; while there is normally a movement of mass flux across the boundary, the overall concentration is most often discontinuous, since the individual concentrations on the coating and in the solution are different from each other. To circumvent this issue, two separate concentrations, i.e. concentration on the solution side (C_A^s) and on the fiber side (C_A^f), have been specified (shown in Figure S1). Then, the concentrations are coupled using an equilibrium relationship, i.e., a partition coefficient ($K_{fs} = C_A^f/C_A^s$). In the present analysis, the value of the stiff-spring velocity term, *M,* was considered as 1000 m/s, since it provided sufficient mass exchange at the coating/solution interface.

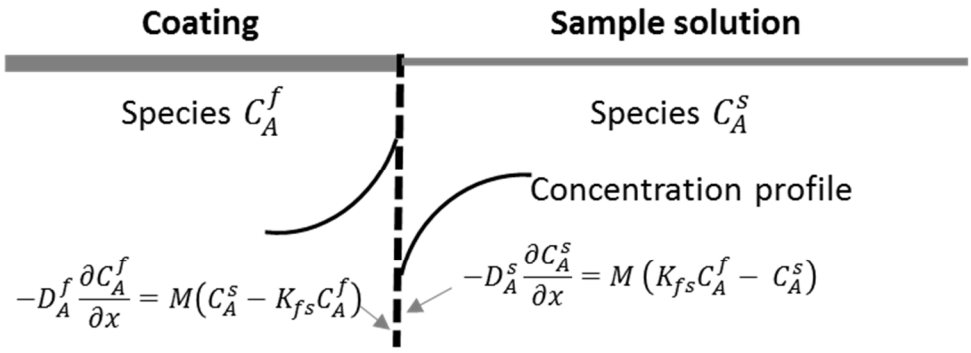

Figure S1. Boundary conditions used for mass transport in the coating/solution interface. Here, *M* is stiff-spring velocity term, K_{fs} is the fiber-solution partition coefficient, D_A^f and D_A^s are the diffusivity coefficient of analyte (A) in fiber and solution phase, respectively.

Model validation: fitting experimental data with the model under static condition

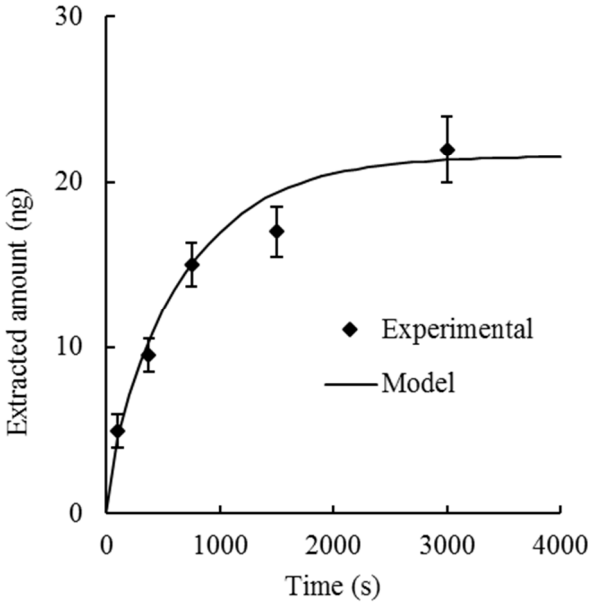

Figure S2. The proposed computational model simulation results were fitted with the experimental data obtained from the absorption profile of an unstirred (static conditions), small volume of benzene solution (100 µl) by a 56 µm thick PDMS coated fiber reported by Louch *et al.*[1] Here, D_A^s: 1.08×10^{-9} m^2/s, D_A^f: 2.8×10^{-10} m^2/s, C_A^s :0.0128 mol/m^3, K_{fs}: 125. The error bars represent standard deviations (n=3).

Model validation: fitting experimental data with the model for various coating thickness

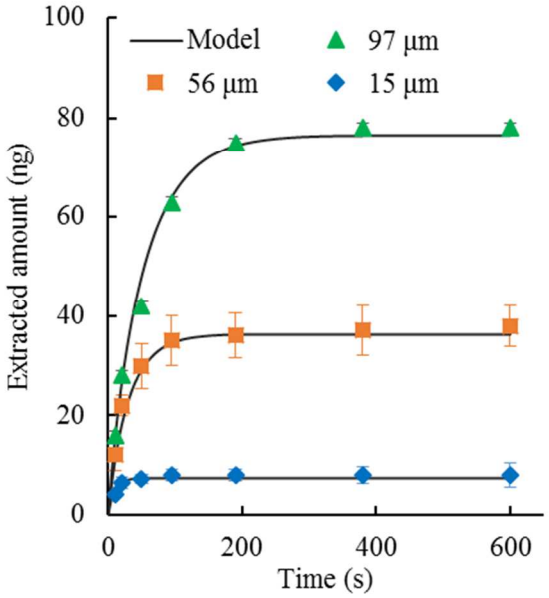

Figure S3. Effect of coating thickness on the extraction of benzene at the stirring speed of 2500 rpm. Three different coating thickness, 97, 56 and 15 µm were compared by keeping the same fiber core diameter at 55 µm. Here, D_A^s: 1.08×10^{-9} m^2/s, D_A^f : 2.8×10^{-10} m^2/s, C_A^s :0.0128 mol/m^3, K_{fs}: 125. The error bars represent standard deviations (n=3).

Confirmation of diffusion controlled kinetics

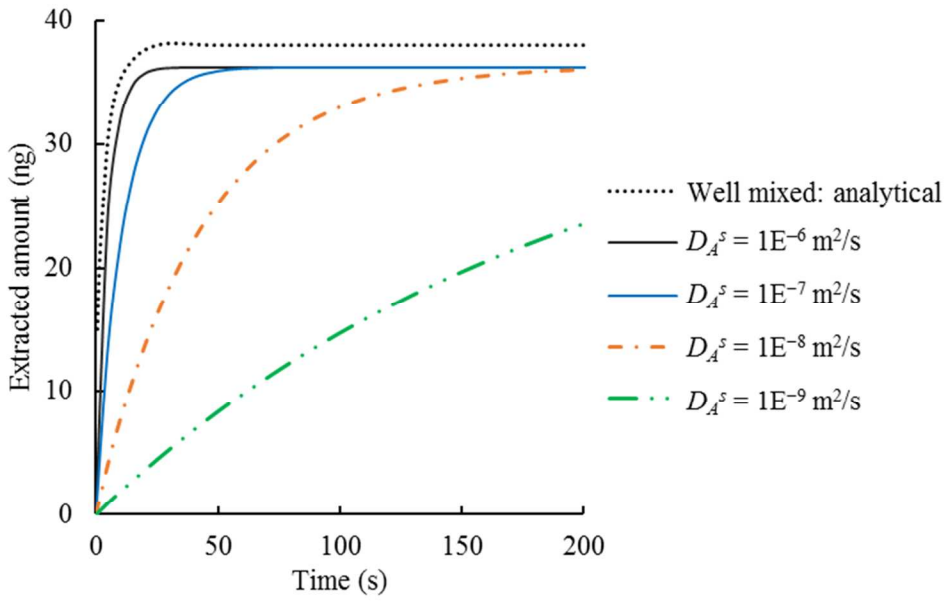

Figure S4. The extracted amount of benzene in fiber coating as a function of time for various values of the analyte diffusion coefficients (D_A^s = 1E^{-6} to 1E^{-9}) in sample solution. The equilibration time obtained for the D_A^s = 1E^{-9} provided similar equilibration time obtained from the well-mixed case of exact solution described by Louch *et al.*[1] Here, D_A^f : 2.8×10^{-10} m^2/s, C_A^s :0.0128 mol/m^3, K_{fs}: 125 and the coating thickness was 56 µm. For the present simulation, the convection was set zero (static conditions).

Dependence of extraction kinetics on the changes in individual values of k_f and k_r

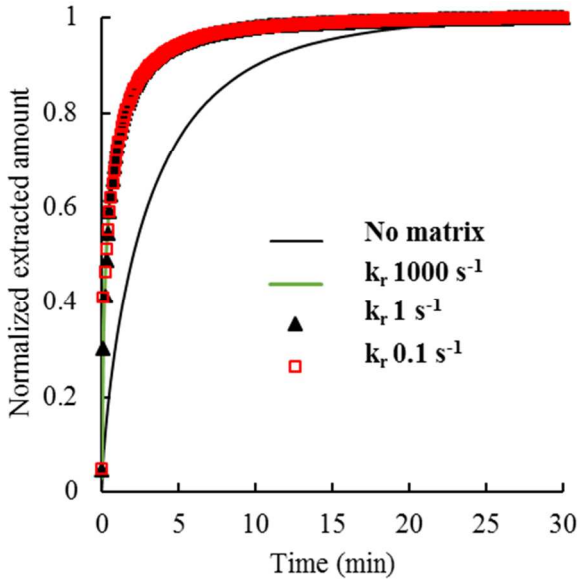

Figure S5. Model simulation results obtained for chlorpromazine binding to bovine serum albumin (BSA) of K_D of 5.4×10^{-4} M with different k_f and k_r values. The k_f values were calculated based on the equation $K_D = k_r / k_f$. The influence of the different physically relevant k_r values on the equilibration time was negligible. For all these experiments, $\beta >> 1$ and $\gamma << 1$. The convection was set zero (static conditions). All other model parameters are presented in Table S1.

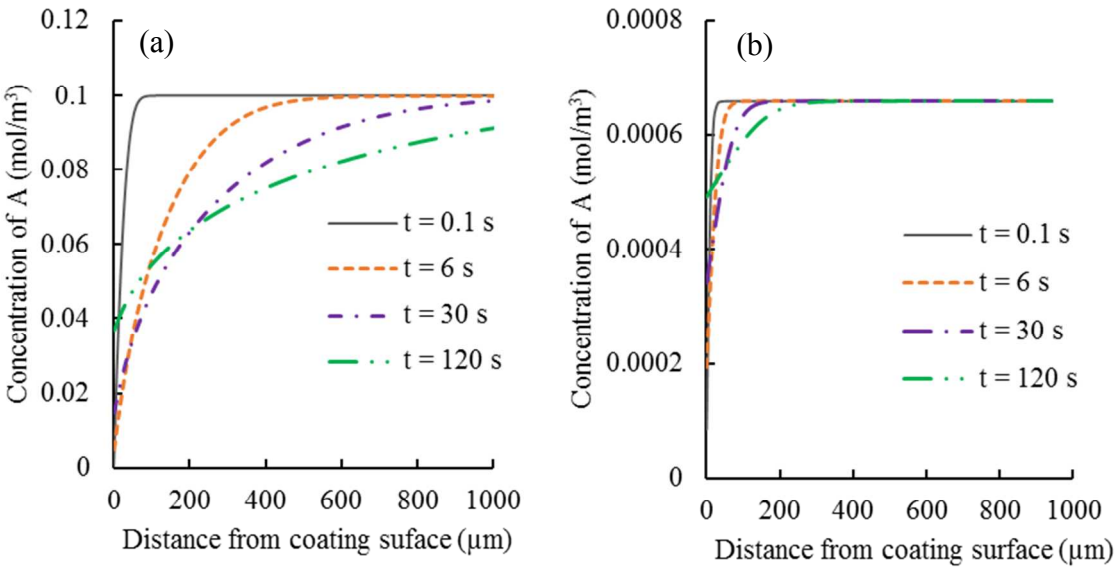

Figure S6. Concentration profiles of the analyte as a function of distance from the coating surface at different extraction times. Model simulation without adding matrix into analyte of concentration 100 uM (a). Model simulation with the presence of 250 uM matrix component of strong (K_D = 10^{-6} M) binding affinity. The convection was set zero (static conditions). All other parameters were kept constant, as shown in Table S1.

Scenario two: retardation of uptake kinetics controlled by diffusion

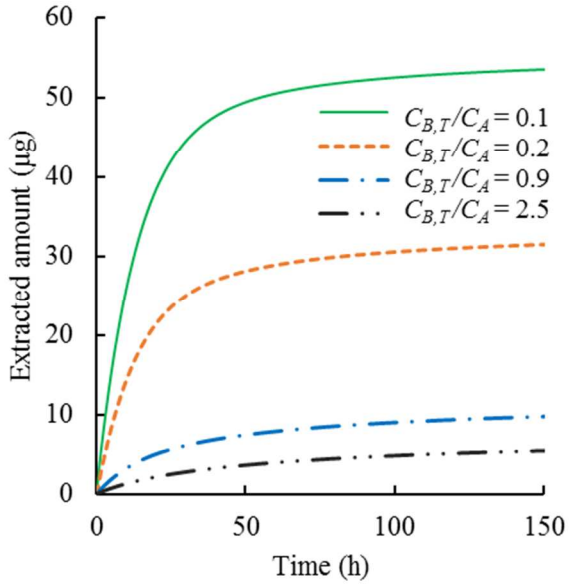

Figure S7. Model simulation of the extraction time profile at different ratio of binding matrix component (BSA) to analyte (chlorpromazine). The concentration of the binding matrix component ($C_{B,T}$) was kept constant at 100 µM and the free analyte concentration (C_A) was varied from 40 µM to 900 µM. The binding strength (K_D) was kept constant at $1E^{-5}$. The convection was set zero (static conditions). All other model parameters are shown in Table S2.

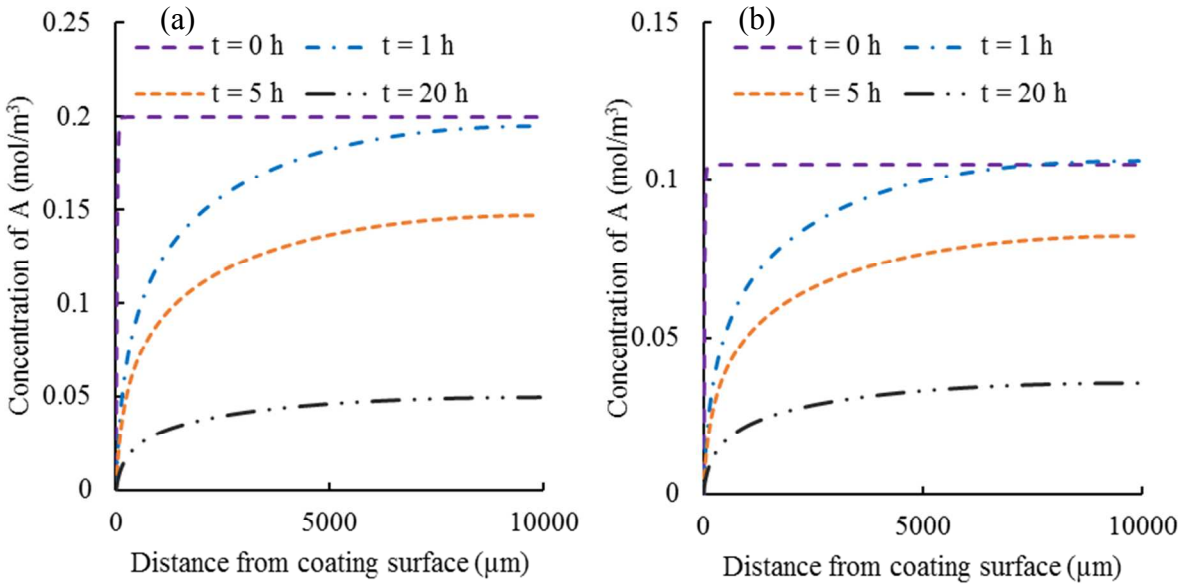

Figure S8. Concentration gradients of the analyte as a function of distance from the coating surface at different extraction times. Model simulation without adding binding matrix component into analyte concentration of 110 uM (a). Model simulation with the presence of

100 uM matrix component of binding affinity, K_D = 10^{-5} M. The convection was set zero (static conditions). All other parameters were kept constant, as shown in Table S3.

Scenario three: retardation of uptake kinetics controlled by unbinding rate (k_r)

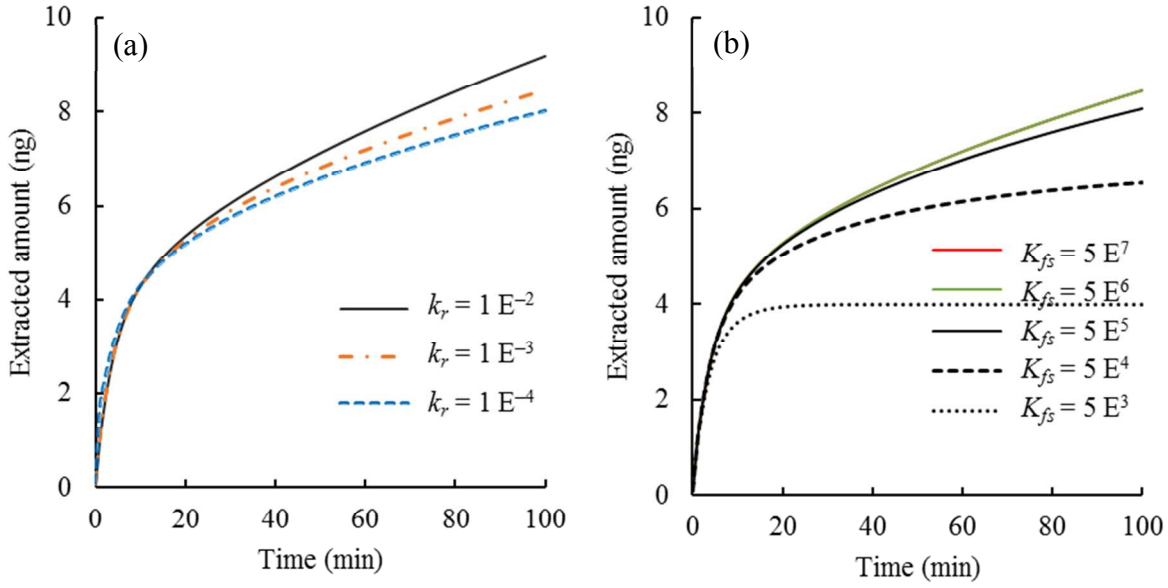

Figure S9. Retardation of uptake kinetics for the scenario three. Effect of unbinding constant (k_r) on the uptake kinetics of an analyte (for example, stanozolol) with the presence of a binding matrix component, (a). Extraction time profile is affected by the value of K_{fs} at k_r = 1E^{-3}, (a). Effect of K_{fs} on the second stage of kinetics for the scenario three, (b). Here, K_D = 5E^{-9} M and C_A = 5.1 µM, $C_{B,T}$ = 100 µM and L = 1 mm. The convection was set zero (static conditions). All other parameters are presented in Table S3.

Table S1. Parameters used for pyrene and chlorpromazine extraction by PDMS and polyacrylate coating respectively.

Symbols	Pyrene[4]	chlorpromazine[5]	Units	Definition
K_D	1.17E^{-7}	5.5E^{-5}	M	Equilibrium dissociation constant
k_f	8.58E^{6}	7.3E^{4}	M^{-1}s^{-1}	Forward rate constant
k_r	1	3.96	s^{-1}	Reverse rate constant
C_A	1.0	100.0	µM	Concentration of analyte
C_B	0.47, 1.4, 23.34	600.0	µM	Concentration of matrix (HSA)

K_{fs}	$1.95E^{4}$	$7.3E^{2}$		Fiber distribution constant
D_A^s	$4.37\ E^{-6}$	$4.3E^{-5}$	cm^2s^{-1}	Diffusivity of analyte in sample
D_A^f	$D_A^s/6$	$6.50E^{-11}$	cm^2s^{-1}	Diffusivity of analyte in fiber
D_{AB}	$5.9\ E^{-7}$	$1.0E^{-7}$	cm^2s^{-1}	Diffusivity of Analyte-matrix in solution
Rc	55	55	μm	Radius of fiber core
Rf	28.5	35	μm	Coating thickness
L	10	10	mm	Radius of sample vessel

Table S2. Parameters used for model simulation of scenario two: retardation of uptake kinetics under diffusion controlled kinetics.

K_D	$5.0\ E^{-5}$	nM	Equilibrium dissociation constant
k_f	$2.0\ E^{4}$	$M^{-1}s^{-1}$	Forward rate constant
k_r	1	s^{-1}	Reverse rate constant
C_A	$1.2\ E^{-4}$	M	Concentration of analyte
C_B	$2.0\ E^{-4}$	M	Concentration of matrix (HSA)
K_{fs}	$5.0\ E^{7}$		Fiber distribution constant
D_A^s	$4.3\ E^{-5}$	cm^2s^{-1}	Diffusivity of analyte in sample
D_A^f	Ds/6	cm^2s^{-1}	Diffusivity of analyte in fiber
D_{AB}	$1.0\ E^{-7}$	cm^2s^{-1}	Diffusivity of Analyte-matrix in solution
Rc	55	μm	Radius of fiber core
Rf	10	μm	coating thickness
L	10	mm	Radius of sample vessel

Table S3. Parameters used for model simulation of scenario three: retardation of uptake kinetics under unbinding controlled kinetics.

K_D	$5.0\ E^{-9}$	nM	Equilibrium dissociation constant
k_f	$2.0\ E^{6}$	$M^{-1}s^{-1}$	Forward rate constant
k_r	$1.0\ E^{-2}$	s^{-1}	Reverse rate constant
C_A	$1.1\ E^{-4}$	M	Concentration of analyte
C_B	$1.0\ E^{-4}$	M	Concentration of matrix (HSA)
K_{fs}	$5.0\ E^{7}$		Fiber distribution constant
D_A^s	$4.3\ E^{-5}$	cm^2s^{-1}	Diffusivity of analyte in sample

D_A^f	Ds/6	cm^2s^{-1}	Diffusivity of analyte in fiber
D_{AB}	$1.0E^{-7}$	cm^2s^{-1}	Diffusivity of Analyte-matrix in solution
Rc	55	μm	Radius of fiber core
Rf	10	μm	coating thickness
L	1	mm	Radius of sample vessel

References

1. Louch, D.; Motlagh, S.; Pawliszyn, J. *Anal. Chem.* **1992,** *64*, 1187-1199.