Supporting Information

Numerical modeling of Solid Phase Microextraction focused on uptake kinetics

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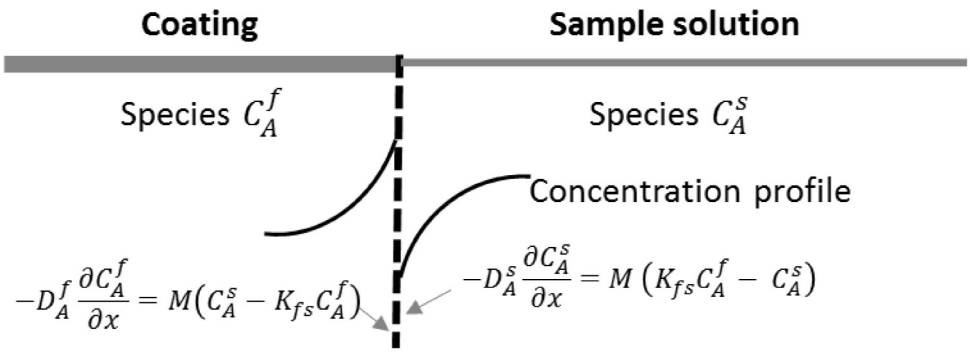

Figure SI- 1. Boundary conditions used for mass transport in the coating/solution interface.

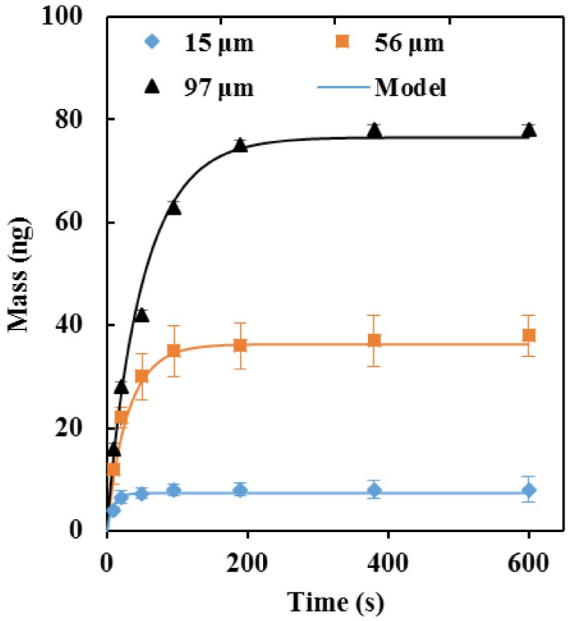

Figure SI- 2. Effect of coating thickness on the extraction of benzene at the maximum stirring speed (2500 rpm). Three different coating thickness (97, 56 and 15 µm) by keeping the same fiber core diameter (55 µm) was compared.

1.

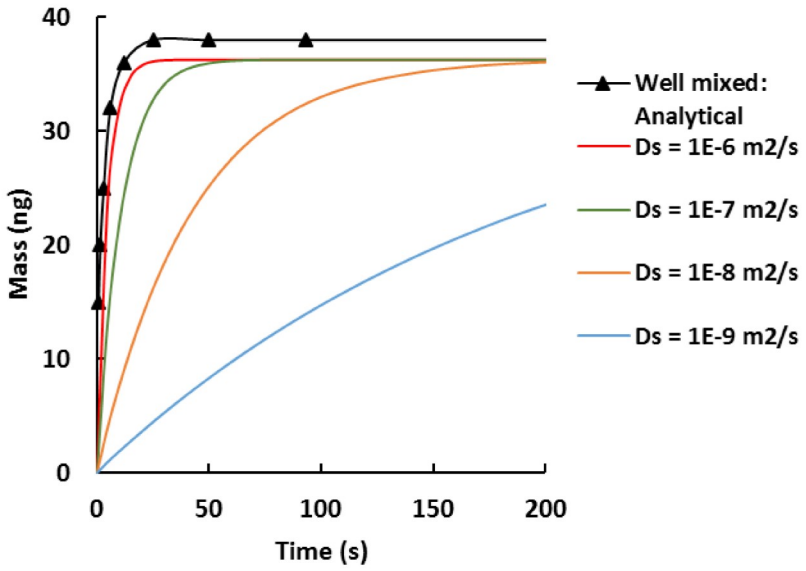

Figure SI- 3. The extracted amount in fiber coating as a function of time for various values of the analyte diffusion coefficient in sample solution. The symbols and lines correspond, respectively, to analytical (well-mixed case) and finite element results.

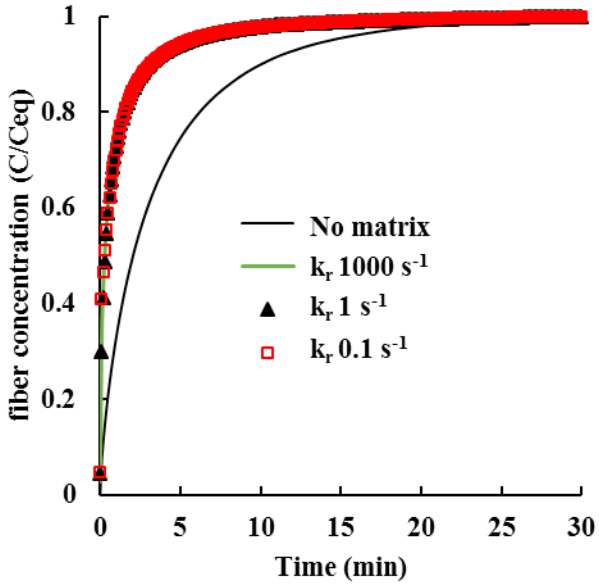

Figure SI- 4. Simulation results for chlorpromazine (K_D of 5.4×10^{-4} M) with different k_f and k_r values. k_f values are calculated based on the equation $K_D = k_r / k_f$. The influence of the different physically relevant kr values on the enhancement of the extraction rate was negligible. For all these experiments, $\beta >> 1$ and $\gamma << 1$.

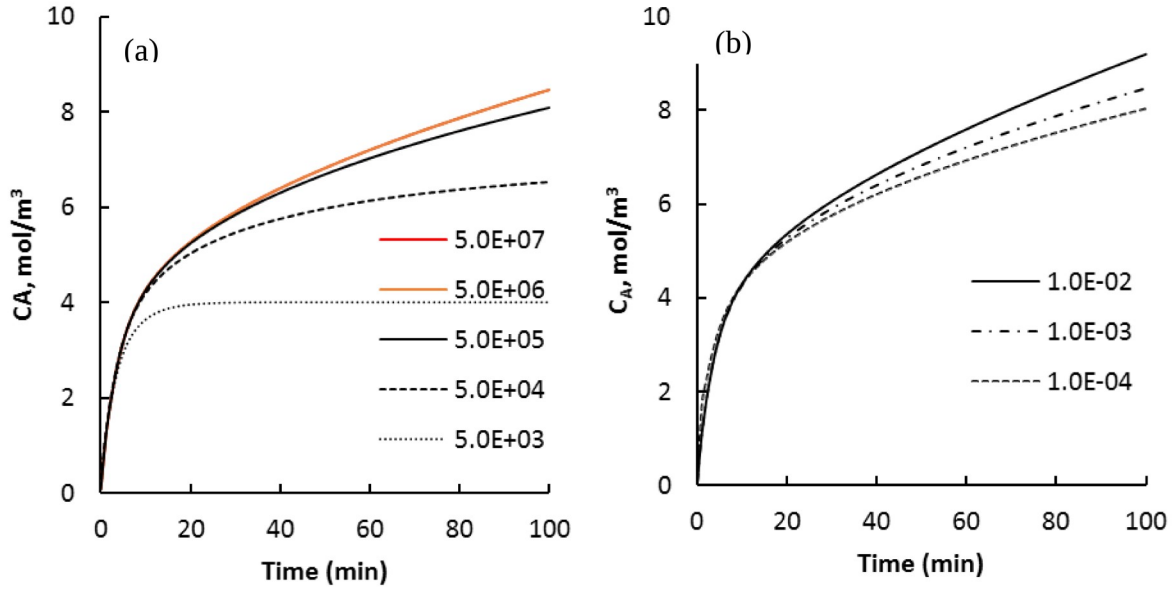

Figure SI- 5. Extraction time profile is affected by the value of K_{fs} at k_r = 1e^{-3}, (a). The effect of k_r on extraction time profile at K_{fs} = 5 e^{-5}, (b).

Table S-1. Parameters used for pyrene and chlorpromazine extraction by PDMS and polyacrylate coating respectively.

Symbols	Pyrene[4]	chlorpromazine[5]	Units	Definition
K_d	1.17E-07	5.5E-05	M	Equilibrium dissociation constant
k_f	8.58E+06	7.3E+04	$M^{-1}s^{-1}$	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+04	7.3E+02		Fiber distribution constant
D_s	4.37E-06	4.3E-05	cm^2s^{-1}	Diffusivity of analyte in sample
D_f	Ds/6	6.50E-11	cm^2s^{-1}	Diffusivity of analyte in fiber
D_{AB}	5.90E-07	1.0E-07	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 SI-2. parameters for heigher Kd case (diffusion controlled).

K_d	5.0E-05	nM	Equilibrium dissociation constant
k_f	2.0E+04	$M^{-1}s^{-1}$	Forward rate constant
k_r	1.0E+00	s^{-1}	Reverse rate constant
C_A	1.2E-04	M	Concentration of analyte
C_B	2.0E-04	M	Concentration of matrix (HSA)
K_{fs}	5.0E+07		Fiber distribution constant
D_s	4.3E-05	cm^2s^{-1}	Diffusivity of analyte in sample
D_f	Ds/6	cm^2s^{-1}	Diffusivity of analyte in fiber
D_{AB}	1.0E-07	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 SI-3. Parameters for lower Kd (unbinding controlled)

Kd	5.0E-09	nM	Equilibrium dissociation constant
kf	2.0E+06	$M^{-1}s^{-1}$	Forward rate constant
kr	1.0E-02	s^{-1}	Reverse rate constant
CA	1.1E-04	M	Concentartion of analyte
CB	1.0E-04	M	Concentartion of matrix (HSA)
Kfs	5.0E+07		Fiber distribution constant
Ds	4.3E-05	cm^2s^{-1}	Diffusivity of analyte in sample
Df	Ds/6	cm^2s^{-1}	Diffusivity of analyte in fiber
DAB	1.0E-07	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