Supporting information

Calibrant Free Sampling and Enrichment with Solid-Phase Microextraction: Computational Simulation and Experimental Verification

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MATHEMATICAL MODEL

Analyte transport in sample solution

The analytes are transported by diffusion and convection in the bulk solution. According to the Fick's law, the following mass balances can be formulated to describe the time-dependent mass transport model for the present system:

$$\frac{\partial C_A}{\partial t} + \boldsymbol{u} \cdot \nabla C_A = \nabla \cdot (D_s \nabla C_A) \qquad 1$$

where C_A denote the concentrations (mol m^{-3}) of the analyte A in the bulk solution phase; D_s is the diffusivity coefficient (m^2 s^{-1}) in the solution phase; $\boldsymbol{u}$ denotes the velocity field (m s^{-1}) and that is obtained from the solution of the momentum transport model governed by the Navier-Stokes equations.

Adsorption on the surface of extractants

Previous studies have shown that Langmuir adsorption isotherm describes equilibrium analyte extraction by solid coatings.[11, 12] The Langmuir isotherm model uses the active sites concept in the adsorption expression to describe the effect of the adsorption rate as a function of the coverage of the coating. Therefore, this model has been used in this study to develop the theoretical description of the adsorption process. Adsorption is treated as a one-step reversible reaction where an analyte molecule A in solution (of bulk concentration C) reacts with the active site of the sorbent S for adsorption on the surface to yield an adsorbed complex AS immobilized onto the active sites of the coating, i.e.

$$\mathrm{A} + \mathrm{S} \underset{k_{des}}{\overset{k_{ads}}{\rightleftharpoons}} \mathrm{AS} \qquad 2$$

The constants k_{ads} and k_{des} represent the rate constants of adsorption and desorption of the analyte onto the active sites, respectively. The maximum attainable surface concentration of the immobilized complex is Γ_{max} (mol cm^{-2}); the surface concentration at time t is $\Gamma(t)$. Therefore, the free active site concentration at any time t is given by Γ_{max} - $\Gamma(t)$. Accordingly, the kinetics of the process is described as follows: the mass balance for adsorbed analyte at the coating surface, including surface diffusion and the reaction for its formation, can be described by the following equation,

$$\frac{\mathrm{d}\Gamma(t)}{\mathrm{d}t} = D_A^e \nabla^2 C_A^e + k_{ads} C_A(t)\left(\Gamma_{max} - \Gamma(t)\right) - k_{des}\Gamma(t) \qquad 3$$

where D_A^e and C_A^e are the diffusion coefficient and the concentration of the analyte A at the extractant surface, respectively, C_A is the free analyte concentration in sample solution at time t.

The ratio of the adsorption and desorption constants k_{ads}/k_{des} determines the equilibrium constant K (Eq. 4). As the adsorption progresses, $\Gamma_{max} - \Gamma(t)$ decreases while $\Gamma(t)$ increases until the equilibrium is reached. If we ignore the surface diffusion term, assume $d\Gamma(t)/dt = 0$ at equilibrium and $C_A^{eq} = C_A^0$ (i.e. the initial concentration of A) in the eq. 3, an analytical expression for the adsorbed centration of the analyte equilibrium (Γ_{eq}) can be obtained (eq. 4).

$$K = \frac{k_{ads}}{k_{des}} = \frac{\Gamma_{eq}}{C_A^0(\Gamma_{max} - \Gamma_{eq})} \qquad 4$$

Considering the surface area (cm^2) of coating, Γ (nmol cm^{-2} or ng cm^{-2}) can be modified as follows:

$$\mathrm{n_{eq}} = \frac{n_{max} C_A^0}{1/K + C_A^0} \qquad 5$$

where n represents the amount of analyte (nmol or ng).

Since eq. 3 includes the sample bulk concentration C_A of analyte, it must be solved in combination with the mass transport equation in the sample. The coupling between the concentration distribution in the bulk sample (2D, eq. 1) and the concentration distribution at the surface (1-D, eq. 3) is obtained by imposing a boundary condition for eq. 1. Boundary condition at the reaction surface is given in the term of mass flux,

$$-e \cdot (C_A v - D_A \nabla C_A) = k_{ads} C_A(t)\big(\Gamma_{max} - \Gamma(t)\big) - k_{des}\Gamma(t) \qquad 6$$

where e is the unit normal vector to the surface. The remaining boundary conditions for equation (1) are as follows:

At time $t = 0$, $C_A = 0$ and $C_A^s = 0$

For all $t > 0$,

At the cylinder's inlet, the analyte concentration was fixed at $C_A = C_A^0$

Insulation is applied to at the walls of the cylinder, i.e.:

$$-\hat{n} \cdot (C_A \boldsymbol{u} - D_A \nabla C_A) = 0 \qquad 7$$

There is no diffusive mass flux at the outlet of the cylinder (analyte is removed by convection only):

$$-\hat{n} \cdot (-D_A \nabla C_A) = 0 \qquad 8$$

CONCENTRATION PROFILE IN THE RETRACTED SPME DEVICE:

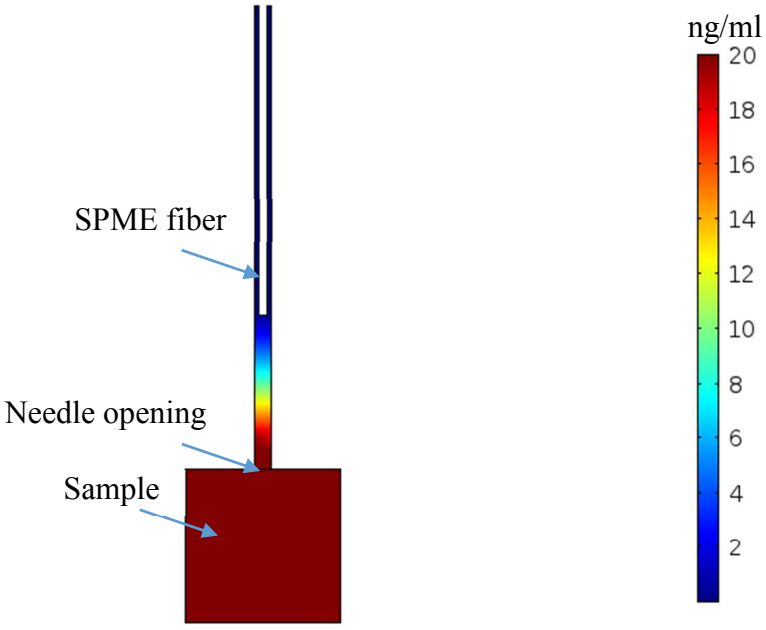

Figure S 1. Concentration profile with a SPME fiber in a needle. For the simulation, the fluid velocity was set at 10 cm s^{-1} with H = 250 µm and Z = 5 mm.

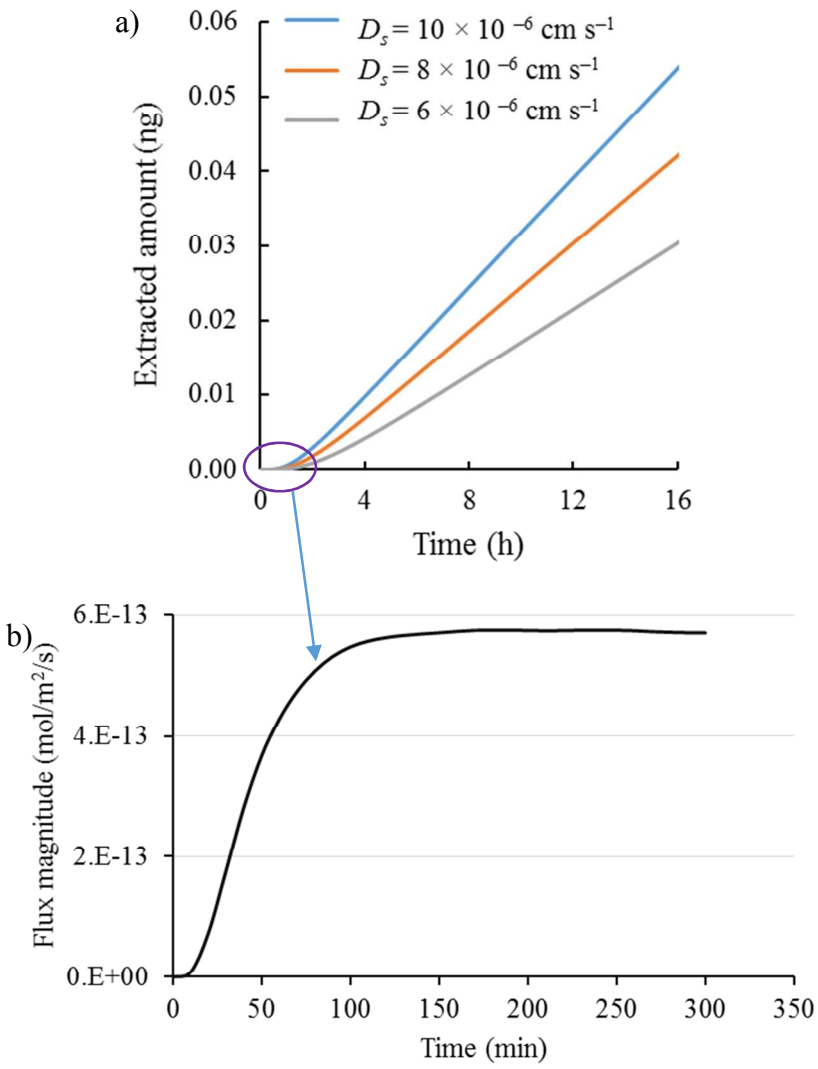

Figure S 2. (a) Dependence of diffusion coefficient value of analyte on the extraction time profiles obtained from a retracted SPME device. Flow velocity was set at 0.2 cm s^{-1} and analyte concentration was set at 20 ng ml^{-1} (b). Time to reach steady state concentration or constant flux magnitude. Therefore, response time is much shorter than the linear regime of the extraction time profile shown in Figure S 2 a.

Table S1. Model parameters used in the simulations.

Symbol	Name	Units
D_s	Diffusion coefficient in solution	$cm^2\ s^{-1}$
D_e	Diffusion coefficient of analyte in the coating	$cm^2\ s^{-1}$
F	Flux	$ng\ s^{-1}$
K	Equilibrium partition coefficient between coating surface and sample solution	$liter\ mol^{-1}$
k_{ads}	Rate constant of adsorption on surface	s^{-1}
k_{des}	Rate constant of desorption from surface	s^{-1}
A_s	Surface area of extractant	m^2
K_a	Association constant between analyte and matrix component	M^{-1}
k_f	rate constant for forward reaction	$M^{-1}\ s^{-1}$
k_r	Rate constant for reverse reaction	s^{-1}
Γ_{max}	Maximum surface concentration	$ng\ m^{-2}$
C_A	Concentration of analyte in extractant	$ng\ m^{-3}$
C_B	Concentration of binding component in sample	$ng\ m^{-3}$
C_{AB}	Concentration of analyte-matrix component complex in sample	$ng\ m^{-3}$

Table S2. Quantitative evaluation of the correspondence between the numerical model and the experimental data.

Figure Number	Root mean square error (RMSE)
Figure 2b	
benzene	3.3×10^{-3}
toluene	2.7×10^{-3}
ethylbenzene	4.5×10^{-3}
o-xylene	3.5×10^{-3}
Figure 3c (sampling rate, ml/s)	2.6×10^{-4}
Figure 8 (Chen model)	1.27
Figure 8 (Numerical model)	0.92

$$RMSE = \sqrt{\frac{\sum(n_{(numericla\ solution)} - n_{(experimental\ data)})^2}{number\ of\ data\ points}}$$