Supplementary Materials

S1. Constraints on Extraction Time for Probing Concentrations with One Phase Only

S1.1. Extraction from adjacent phase to fiber

Upon insertion of the extractive fiber into either phase, diffusion of the analyte to the fiber proceeds due to the perturbation in the analyte concentration of that phase. This perturbation travels away from the fiber at a rate that is directly proportional to the diffusion coefficient of that substrate in that phase. A common way to characterize the propagation of the perturbation is through the time scale, \( \frac{L^2}{D} \), where \( L \) is some distance and \( D \) is the diffusion coefficient. We use this relation to examine HS-SPME versus DI-SPME with respect to the rates of mass transport in the two phases and the geometries of the experimental setups.

Consider the HS-SPME and DI-SPME setups shown in Fig. 1. The closest distance from fiber to adjacent phase in our experiments was no less than 1 mm. If the fiber is in the vapor, then the time scale for the diffusive perturbation to reach the vapor–liquid interface is approximately \( \frac{(0.1 \text{ cm})^2}{(0.072 \text{ cm}^2/\text{s})} = 0.14 \text{ s} \). The value of 0.072 cm²/s is the diffusion coefficient of heptane in air, which is the fastest-diffusing analyte in this study. If the fiber is in the liquid, then the time scale for the diffusive perturbation to reach the vapor–liquid interface is approximately \( \frac{(0.1 \text{ cm})^2}{(7.5 \times 10^{-6} \text{ cm}^2/\text{s})} = 22 \text{ min} \), where \( 7.5 \times 10^{-6} \text{ cm}^2/\text{s} \) is the diffusion coefficient in water of heptane. Since the extraction times were 1 min and 5 min for our HS-SPME and DI-SPME partition coefficient experiments, respectively, extraction from the adjacent phase must be considered for HS-SPME, and it can be considered negligible for DI-SPME. Thus, we attempt to estimate the effect of this process for the HS-SPME partition coefficient experiments next.
S1.2. Extraction from liquid phase to gas phase over HS-SPME sampling times

Rates of time dependent diffusion can be used to estimate the erroneous signal associated with solute transport from the liquid phase to the headspace during HS-SPME extraction. The concentration of the analyte in the liquid in this case is given by

\[ c_t = c_{t0} \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-x^2} \, dx \]  \hspace{1cm} (S1.2.1)

where \( c_{t0} \) is the initial liquid concentration, \( x \) is a spatial coordinate with its origin at the vapor–liquid interface and pointing down into the liquid, \( t \) is time, and \( D \) is the diffusion coefficient of the analyte in the liquid.

The extra analyte extracted from the liquid phase, \( n_e \), as a function of time is given by

\[ n_e(t) = \int_0^\infty (c_{t0} - c_t(x,t))A \, dx, \]  \hspace{1cm} (S1.2.2)

where \( A \) is the cross-sectional area of the column of liquid. The initial amount of analyte in the liquid is \( n_{t0} = HA c_{t0} \), where \( H \) is the height of the column of liquid. Combining this definition with eqs (S1.2.2) and (S1.2.1) and solving the integral, we find that

\[ \frac{n_e}{n_{t0}} = \sqrt{\frac{4Dt}{\pi H^2}}. \]  \hspace{1cm} (S1.2.3)

Since \( n_{t0} = n_{v0} V_v/(K_v V_v) \), and \( H \) is the product of the fill fraction \( f \) and the total sample height \( H_t \), the ratio of extra analyte extracted from the liquid phase to the initial amount of analyte in the vapor phase is

\[ \frac{n_e}{n_{v0}} = \frac{V_v}{K_v V_v} \sqrt{\frac{4Dt}{\pi f^2 H_t^2}}. \]  \hspace{1cm} (S1.2.4)
Ideally, this ratio should be small, so that the apparent, measured $K_{v\ell}$ will not be significantly greater than the actual $K_{v\ell}$. If we want $n_{e}/n_{v0}$ to be less than, for example, 1%, we can calculate the maximum sampling time, $t_{\text{max}}$ required to achieve this target. This time is given explicitly by

$$t_{\text{max}} = \frac{\pi}{4D} \left(1 - f\right) H_{i} K_{v\ell} \frac{n_{e}}{n_{v0}}^2.$$  

(S1.2.5)

When the error $n_{e}/n_{v0}$ is significant, the apparent partition coefficient, $K_{v\ell}^{\text{app}}$, can be estimated from the following modification to the equation $A = k_{v\ell}$, where method response (e.g., chromatographic peak area, $A$) is directly proportional to the vapor concentration, $c_{v}$:

$$A = k c_{v0} \left(1 + \frac{n_{e}}{n_{v0}}\right)$$  

(S1.2.6)

where the subscript '0' is added to $c_{v}$ to indicate the initial vapor concentration. Eqn (S1.2.4) is used to evaluate $n_{e}/n_{v0}$ and the result is substituted into eqn (4) to determine $K_{v\ell}^{\text{app}}$ from measurements at two fill fractions $f_{1}$ and $f_{2}$. The result can be expressed as

$$K_{v\ell}^{\text{app}} = \frac{N f_{1} \left(1 - f_{1}\right) - f_{2}}{1 - f_{2} - N},$$  

(S1.2.7)

where

$$N = \kappa (1 - f_{2}) \frac{M(f_{1})}{M(f_{2})}.$$  

(S1.2.8)

Here we have defined the function

$$M(f) = \frac{\sqrt{\pi} (1 - f) K_{v\ell} + 2\sqrt{D \ell f_{i} H_{i}}}{f_{i} (1 - f_{i}) K_{v\ell}}.$$  

(S1.2.9)
S2. Analysis of Magnification of Uncertainty

S2.1. Linear approximation model for magnification of uncertainty

The analysis of uncertainty begins with the determination of $K_v$ from measurements of the slopes $S_1$ and $S_2$ in eqn (4), with $R=S_1/S_2$.

The error in $K_v$ arising from measurements of $S_1$ and $S_2$ may be approximated as in eqn (9):

\[
\sigma_{K_v}^2 \approx \sigma_{S_1}^2 \left( \frac{\partial K_v}{\partial S_1} \right)^2 + \sigma_{S_2}^2 \left( \frac{\partial K_v}{\partial S_2} \right)^2 \tag{S2.1.1}
\]

which, using $R=S_1/S_2$ and

\[
\frac{\partial K_v}{\partial S_j} = \frac{\partial R}{\partial S_j} \left( \frac{\partial R}{\partial K_v} \right)^{-1}, \tag{S2.1.2}
\]

may be rearranged to

\[
\sigma_{K_v}^2 \approx R^2 \left( \frac{\partial R}{\partial K_v} \right)^{-2} \left( \frac{\sigma_{S_1}^2}{S_1^2} + \frac{\sigma_{S_2}^2}{S_2^2} \right). \tag{S2.1.3}
\]

Since $(\sigma_R/R)^2 = [(\sigma_{S_1}/S_1)^2 + (\sigma_{S_2}/S_2)^2]$, eqn (S2.1.3) may be reexpressed as

\[
\frac{\delta}{\varepsilon} = \frac{\sigma_{K_v}/K_v}{\sigma_R/R} = \frac{R}{K_v} \left( \frac{\partial R}{\partial K_v} \right)^{-1}. \tag{S2.1.4}
\]

The final step is to solve eqn (4) for $R$ and substitute the result into eqn (S2.1.4) to show that the magnification of uncertainty is a function of $f_1, f_2$, and $K_v$ only:

\[
\frac{\delta}{\varepsilon} = \left[ K_v f_1 + f_1 \right] \left[ K_v \left( 1 - f_2 \right) + f_2 \right] \frac{\sigma_{K_v}}{K_v} \left( f_1 - f_2 \right) \tag{S2.1.5}
\]
The dashed lines in Fig. 3, in the text, show how this approximated magnification of uncertainty varies with $K_{v_{1}}$ for two sets of conditions: \{$f_1, f_2\} = \{0.8, 0.2\}$ and \{0.9, 0.1\}.

S2.2. Exact solution for magnification of uncertainty

Using eqn (4), $K_{v_{1}}$ is calculated from $R$ and from the experimental parameters $f_1, f_2$ and $\kappa$. Since $K_{v_{1}}$ must be positive and finite, it is clear from eqn (4) that accurate measurements of $R$ must fall within the domain $R \in [R_{0}, R_{\infty}]$ where

$$R_{0} = \lim_{K_{v_{1}} \to 0} R = \frac{f_{2}}{\kappa f_{1}} \quad (S2.2.1)$$

and

$$R_{\infty} = \lim_{K_{v_{1}} \to \infty} R = \frac{1-f_{2}}{\kappa(1-f_{1})} \quad (S2.2.2)$$

Although our error analysis is of course invariant to the choice of labels number “1” and “2” for the different sample conditions, for the purposes of our argument it is convenient to consider labels such that $f_{1} > f_{2}$. With this choice, we find that $R_{0}$ is a lower bound on $R$, and $R_{\infty}$ is an upper bound.

Equation (S2.1.5) is derived based on a first order linear approximation; however, it is possible to find the exact analytical solution for the propagation of error. Suppose an experiment yields $S_{1} \pm \sigma_{S_{1}}$ and $S_{2} \pm \sigma_{S_{2}}$ (as in Fig. 3). We then find that

$$\sigma_{R} = R\sqrt{\left(\frac{\sigma_{S_{1}}}{S_{1}}\right)^{2} + \left(\frac{\sigma_{S_{2}}}{S_{2}}\right)^{2}}. \quad (S2.2.3)$$
Given a true value of $R$, the measured values contain an error $\varepsilon = \pm \sigma_R / R$, so that $R^{\text{err}} = R(1 + \varepsilon)$. We can then determine the resulting error $\delta = \left( K_{\text{err}}^{\text{eq}} - K_{\text{eq}} \right) / K_{\text{eq}}$ in the partition coefficient, using

$$K_{\text{eq}} = \frac{\kappa R (1 + \varepsilon) f_1 - f_2}{1 - f_2 - \kappa R (1 + \varepsilon) (1 - f_1)} \quad \text{(S2.2.4)}$$

Although in general $\varepsilon$ can be either positive or negative, for values of $R$ approaching $R_0$ or $R_{c}$, respective negative or positive errors will lead to values of $R^{\text{err}}$ outside the physically plausible domain, corresponding to nonphysical values of $K_{\text{eq}}^{\text{err}}$. In our discussion we have considered only those values of $\varepsilon$ such that $R^{\text{err}} \in [R_0, R_{c}]$. The error, $\delta$, can then be calculated for any value of $\varepsilon$ using eqs (S2.2.4) and (4), to yield the magnification of uncertainty $\delta / \varepsilon$, equivalent to the definition given in eqn (10).