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, 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 $(0.1$ $cm)^2/(0.072$ $cm^2/s) = 0.14$ s. The value of 0.072 cm^2/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 $(0.1$ $cm)^2/(7.5 \times 10^{-6}$ $cm^2/s) = 22$ min, where 7.5×10^{-6} cm^2/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

$$c_\ell = c_{\ell 0} \frac{2}{\sqrt{\pi}} \int_0^{x/\sqrt{4D_\ell t}} e^{-\lambda^2} \, d\lambda \qquad (S1.2.1)$$

where $c_{\ell 0}$ 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_ℓ 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

$$n_e(t) = \int_0^\infty \left(c_{\ell 0} - c_\ell(x,t) \right) A \, dx, \qquad (S1.2.2)$$

where A is the cross-sectional area of the column of liquid. The initial amount of analyte in the liquid is $n_{\ell 0} = HAc_{\ell 0}$, 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

$$\frac{n_e}{n_{\ell 0}} = \sqrt{\frac{4D_\ell t}{\pi H^2}} . \qquad (S1.2.3)$$

Since $n_{\ell 0} = n_{v0}V_\ell/(K_{v\ell}V_v)$, 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

$$\frac{n_e}{n_{v0}} = \frac{V_\ell}{K_{v\ell}V_v} \sqrt{\frac{4D_\ell t}{\pi f^2 H_t^2}} . \qquad (S1.2.4)$$

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_{max} required to achieve this target. This time is given explicitly by

$$t_{max} = \frac{\pi}{4D}\left[(1-f)H_t K_{v\ell}\frac{n_e}{n_{v0}}\right]^2 . \tag{S1.2.5}$$

When the error n_e/n_{v0} is significant, the apparent partition coefficient, $K_{v\ell}^{app}$, can be estimated

from the following modification to the equation $A=kc_v$, where method response (e.g.,

chromatographic peak area, A) is directly proportional to the vapor concentration, c_v:

$$A = kc_{v0}\left(1+n_e/n_{v0}\right) \tag{S1.2.6}$$

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 $K_{v\ell}^{app}$ from

measurements at two fill fractions f_1 and f_2. The result can be expressed as

$$K_{v\ell}^{app} = \frac{Nf_1/(1-f_1)-f_2}{1-f_2-N}, \tag{S1.2.7}$$

where

$$N = \kappa(1-f_2)\frac{M(f_1)}{M(f_2)}. \tag{S1.2.8}$$

Here we have defined the function

$$M(f_i) = \frac{\sqrt{\pi}(1-f_i)K_{v\ell}+2\sqrt{Dt}/H_t}{f_i+(1-f_i)K_{v\ell}}. \tag{S1.2.9}$$

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S2. Analysis of Magnification of Uncertainty

S2.1. Linear approximation model for magnification of uncertainty

The analysis of uncertainty begins with the determination of $K_{v\ell}$ from measurements of the slopes

S_1 and S_2 in eqn (4), with $R=S_1/S_2$.

The error in $K_{v\ell}$ arising from measurements of S_1 and S_2 may be approximated as in eqn

(9):

$$\sigma_{K_{v\ell}}^2 \approx \sigma_{S_1}^2 \left(\frac{\partial K_{v\ell}}{\partial S_1} \right)^2 + \sigma_{S2}^2 \left(\frac{\partial K_{v\ell}}{\partial S_2} \right)^2 \qquad (S2.1.1)$$

which, using $R=S_1/S_2$ and

$$\frac{\partial K_{v\ell}}{\partial S_i} = \frac{\partial R}{\partial S_i} \left(\frac{\partial R}{\partial K_{v\ell}} \right)^{-1}, \qquad (S2.1.2)$$

may be rearranged to

$$\sigma_{K_{v\ell}}^2 \approx R^2 \left(\frac{\partial R}{\partial K_{v\ell}} \right)^{-2} \left(\frac{\sigma_{S_1}^2}{S_1^2} + \frac{\sigma_{S_2}^2}{S_2^2} \right). \qquad (S2.1.3)$$

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

$$\frac{\delta}{\varepsilon} = \frac{\sigma_{K_{v\ell}}/K_{v\ell}}{\sigma_R/R} = \frac{R}{K_{v\ell}} \left(\frac{\partial R}{\partial K_{v\ell}} \right)^{-1} \qquad (S2.1.4)$$

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 $K_{v\ell}$ only:

$$\frac{\delta}{\varepsilon} = \frac{\left[K_{v\ell}(1-f_1) + f_1 \right]\left[K_{v\ell}(1-f_2) + f_2 \right]}{K_{v\ell}(f_1 - f_2)} \qquad (S2.1.5)$$

The dashed lines in Fig. 3, in the text, show how this approximated magnification of uncertainty varies with $K_{v\ell}$ 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), $K_{v\ell}$ is calculated from R and from the experimental parameters f_1, f_2 and κ. Since $K_{v\ell}$ 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

$$R_0 = \lim_{K_{v\ell} \to 0} R = \frac{f_2}{\kappa f_1} \qquad \text{(S2.2.1)}$$

and

$$R_\infty = \lim_{K_{v\ell} \to \infty} R = \frac{1 - f_2}{\kappa(1 - f_1)} \qquad \text{(S2.2.2)}$$

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_∞ 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

$$\sigma_R = R \sqrt{\left(\sigma_{S_1} / S_1\right)^2 + \left(\sigma_{S_2} / S_2\right)^2}. \qquad \text{(S2.2.3)}$$

Given a true value of R, the measured values contain an error $\varepsilon = \pm \sigma_R / R$, so that $R^{err} = R(1 + \varepsilon)$. We can then determine the resulting error $\delta = \left(K_{v\ell}^{err} - K_{v\ell} \right) / K_{v\ell}$ in the partition coefficient, using

$$K_{v\ell} = \frac{\kappa R(1 + \varepsilon) f_1 - f_2}{1 - f_2 - \kappa R(1 + \varepsilon)(1 - f_1)} \qquad (S2.2.4)$$

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