Development of a Diffusive Gradients in Thin-Films Passive Sampling Device for PFAS (ER20-1363)

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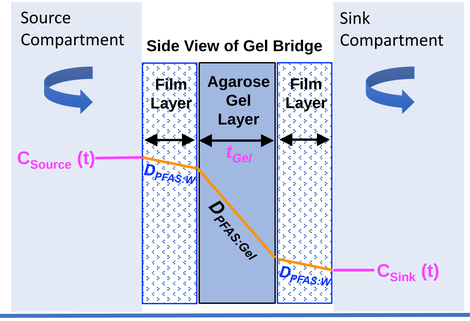
Introduction:

The diffusion coefficient in a hydrogel (D_{Gel}) is the analyte specific constant that equips diffusive gradients in thin-films (DGT) passive sampling devices (PSDs). In this growing realm of research, the two-compartment diffusion cell (2CDC) has been used to measure hundreds of diffusion coefficients for a wide array of analytes ranging from inorganic metals to organic contaminants including PFAS. Despite the prolific use of the 2CDC, no standardization for the device has been developed. Many labs have shown consistent and verified measurements of D_{Gel}, however, lab to lab results show greater variation. In order to better establish the key parameters impacting the measurement of D_{Gel} using a 2CDC, a custom 2CDC was built and the following set of experiments were performed.

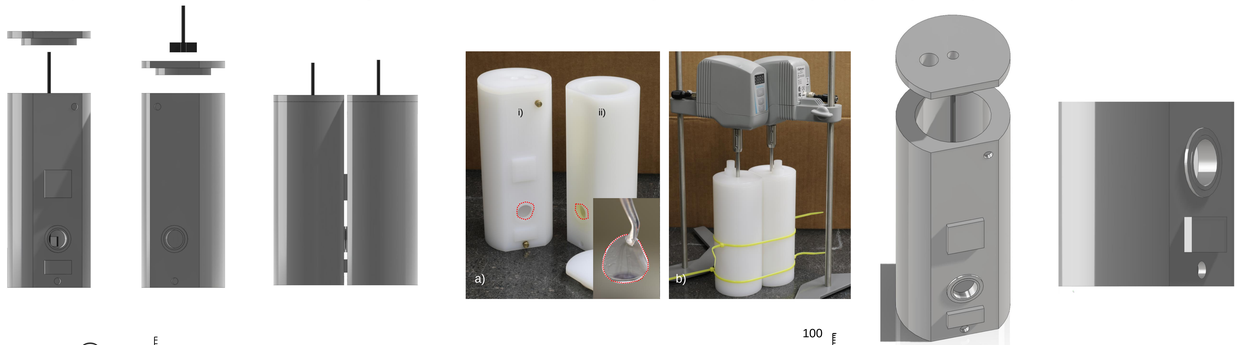
Diffusion Boundary/Film Layer (DBL) Formation:

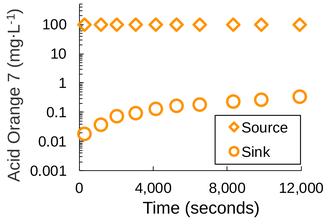
The DBL is generally ignored in the diffusion cell because it is thought to be small relative to the total thickness of the gel. It was hypothesized that this assumption may be violated due to the wall thickness at the orifice which produces a "cave" that could stagnate water, increasing the DBL thickness

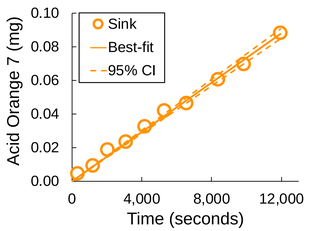


Diffusion Cell Experiments with Dyes → PFAS:

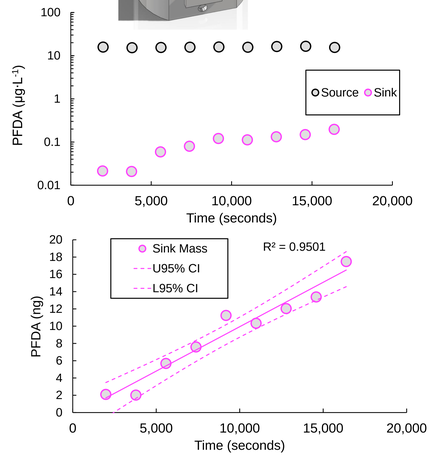
Initial experiments were conducted using PFBS and PFDA in a ultra high molecular weight polyethylene (UHMWPE) 2CDC.





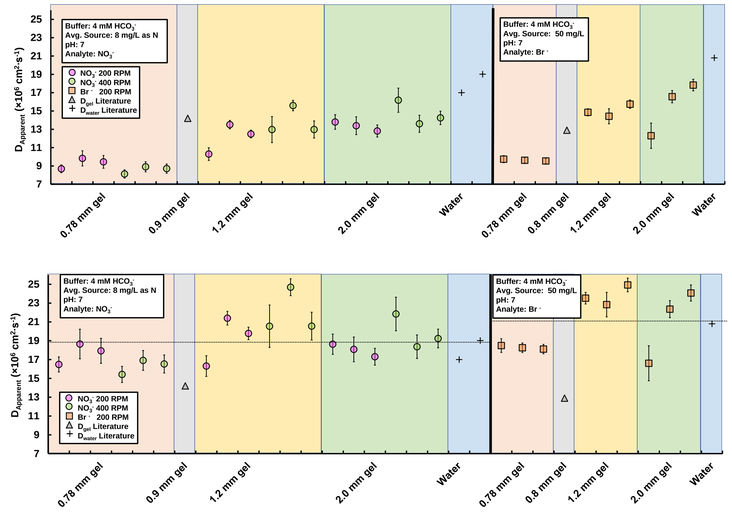


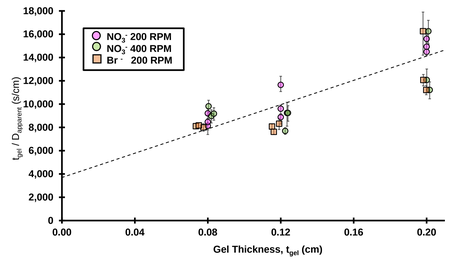
$$Equation\ 1:\ D_{gel} = \frac{\alpha \cdot \Delta g}{A \cdot C}$$



Surrogate Experiments to Measure the DBL Thickness:

To determine the thickness of the DBL that is forming in the 2CDC, three sets of 9 experiments were conducted with bromide (Br^-) and Nitrate (NO_3^-) at mixing rates of 200 and 400 RPM.



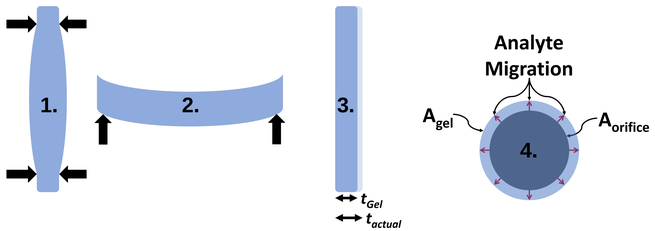


The plot of the nitrate diffusion coefficients at varied gel thicknesses indicates there is something contributing error to the measurement of D producing an apparent diffusion coefficient ($D_{apparent}$) that includes diffusion through a DBL of unknown thickness. To determine the DBL thickness, we can plot the median value of the $t_{Gel}/D_{apparent}$ vs. t_{Gel}. By multiplying the inverse slope of the regression line by its Y-intercept, we can determine the diffusive distance which is unaccounted for in t_{Gel}.

Error Identification:

The error in the initial 2CDC experiments indicated parameters of importance were being overlooked. The following are some of the possible sources of physical error that could be impacting measurements of $D_{apparent}$.

1. Bulging due to clamping
2. Concave shape toward the installation compartment
3. Swelling of the gel $t_{actual} > t_{gel}$
4. Analyte migration diffusive area > $A_{orifice}$



Conclusions:

The measurement of the DBL thickness indicates that a DBL of 0.4 mm is forming in either compartment of the 2CDC. Relative to the thinnest gel thickness of 0.8 mm this indicates a DBL of more than 100% which could significantly skew the D_{Gel} value for any given analyte measured on the 2CDC.

- The DBL is significant in the 2CDC measurements

References

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