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Determination of polydimethylsiloxane (PDMS)-seawater distribution coefficients for polychlorinated biphenyls and chlorinated pesticides by solid-phase microextraction

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ABSTRACT

Despite the growing popularity of solid-phase microextraction (SPME) among the community of analytical chemists, applications of SPME in the measurement of very hydrophobic organic compounds (VHOCs) have remained limited. This is due, in part, to the difficulty of calibrating SPME devices for VHOCs. Here, we present an analytical procedure used to determine the distribution coefficients (K_f values) for a large suite of polychlorinated biphenyl (PCB) congeners and chlorinated pesticides between a polydimethylsiloxane (PDMS) phase (100 μm thickness) and seawater. Losses of analytes to sample containers and stirring bars were accounted for in the determination of K_f . The correlation between $\log K_f$ and $\log K_{ow}$, the octanol-water partition coefficient, was positively linear for PCB congeners with $\log K_{ow}$ up to ~ 6.5 , but became negatively linear for PCB congeners with $\log K_{ow} > 6.5$. When grouped based on the number of chlorines (homolog), $\log K_f$ increased linearly with increasing $\log K_{ow}$ for homologs 3-5 and decreased for homologs 6-10. These findings were inconsistent with existing data acquired using thinner PDMS coatings (7 and 15 μm), which exhibited a positively linear relationship between $\log K_f$ and $\log K_{ow}$ for all PCB congeners. We postulate that the larger PCB congeners cannot readily sorb into the bulk PDMS phase, as would be required to maintain a consistent sorptive capacity for the thick 100 μm fiber coating. This effectively lowers the sorption capacity of PDMS-coated SPME devices for high molecular weight PCB congeners. This hypothesis contributes additional insight toward understanding the mechanism of SPME processes with PDMS phases.

Full Text

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