SCCWRP Annual Report 2001-02

Theoretical considerations on the use of solid phase microextraction with complex environmental samples

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ABSTRACT

Solid phase microextraction (SPME) is a relatively new technique for extraction of organic chemicals from aqueous matrices. However, SPME has been applied mainly to relatively clean samples and polar organic compounds. Its utility in extraction of hydrophobic organics from complex heterogeneous matrices remains to be proven, and the impact of matrix interferences needs to be quantified. In this article, the equations governing the use of equilibrium SPME for environmental samples with complex heterogeneous matrices were derived in terms of parameters commonly measured or estimated by environmental scientists. Parameterization of the SPME equations allowed for the *a priori* prediction of SPME performance as a function of analyte and sample properties, as well as experimental conditions. A theoretical evaluation of SPME was performed for a broad range of realistic scenarios using calculated equilibrium partitioning parameters, and the implications for practical applications were discussed. Potential pitfalls and errors in quantitative measurements were identified and different approaches to SPME calibration were presented. The concept of an optimum minimum volume for the analysis of heterogeneous environmental samples was presented and fully developed. Data from three previous studies were used to validate the correctness of the theoretical framework; the agreement between the measured relative recoveries of a variety of hydrophobic organic chemicals and theoretical predictions was exceptionally good. The results of this study highlight the potential for SPME to be a valuable technique for the measurement of hydrophobic organic contaminants in complex environmental samples. The SPME technique appears to be especially well suited for samples with high solids-to-water ratios and/or large sample volumes. Examples of such applications include sediment interstitial water and *in situ* field measurements, respectively.

Full Text

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