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Dynamic Solid Phase Microextraction (SPME) of Atrazine at PDMS and PA Coated Fibers

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The accumulation rate and equilibrium partitioning behavior of the pesticide atrazine between water and two solid phase microextraction (SPME) fibers, polydimethylsiloxane (PDMS) and polyacrylate (PA), are presented. The more polar PA is found to accumulate atrazine to a greater extent than does PDMS. The solid phase-water partition coefficient, K_{sw}, for atrazine is 210 for PA and 55 for PDMS. The accumulation rate constant increases as the rate of solution stirring is increased. This result confirms that the rate of accumulation of atrazine in both PDMS and PA is limited by diffusion in the aqueous medium. Accordingly, these solid phases are useful for studying the speciation dynamics of atrazine in aqueous media.

1. Introduction

Solid phase microextraction (SPME) has found wide application in extraction of organic target compounds from diverse matrices, including environmental compartments e.g. water (Yang et al., 2007), soil (Gomez-Eyles et al., 2012), sediment (Harwood et al., 2012), air (Toscano et al., 2011), biological samples (Vuckovic et al., 2010) such as blood, urine, whole organisms, as well as many foods (Abdulra'uf et al., 2012). SPME provides selective preconcentration of compounds, which are generally subsequently identified and quantified by chromatography.

SPME fibers comprise an inert core (typically silica, ca. 55 μm diameter) coated with a thin film of a solid phase polymer (film thickness ca. 10 – 100 μm). SPME is based on partitioning of the target compounds between the aqueous sample and a solid polymeric phase. A range of parameters may affect the rate of extraction and the eventual equilibrium partitioning, e.g. the nature of the solid phase and the target compound, the thickness of the solid phase film, temperature, solution convection, ionic strength, pH, presence of complex species, etc. (Valor et al., 1996; Heringa and Hermens, 2003).

Furthermore, depending on the type of solid phase, the solution convection conditions, and the nature of the target compound, the accumulation rate may be limited by (i) diffusion in the solid phase or (ii) diffusion in the aqueous medium (Heringa and Hermens, 2003). In case (i), only the free non-complexed target contributes to the rate of accumulation, whilst in case (ii) complexed target species may enhance the rate of accumulation to an extent determined by their lability (Kramer et al., 2007; Benhabib et al., 2009).

Several solid phases with different sorbent properties are available, and the partition mechanisms may involve both absorption and adsorption (Pawliszyn, 1997; Dugay et al., 1998; Górecki, 1997). In this work we use two solid phases that accumulate organic targets via absorption, namely

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polydimethylsiloxane (PDMS) and polyacrylate (PA). PDMS is relatively nonpolar, whilst PA is relatively polar; both polymers have been applied to extraction of s-triazine herbicides from water (Barnabas et al., 1995; Eisert et al., 1996).
The present work describes the dynamics of accumulation of atrazine at PDMS and PA coated SPME fibers. The extraction-time profiles for the two solid phases are presented, and the rate limiting step for accumulation in the solid phase is identified.

2. Experimental

2.1 Reagents

The herbicide atrazine was obtained from Sigma-Aldrich. The SPME fibers were obtained from Poly Micro Industries (Phoenix, AZ), and comprised a silica core of radius 55 µm coated with PDMS (polymer thickness 28.5 µm) or PA (polymer thickness 30 µm). Analytical grade acetone was from Lab-Scan. The fibers were cleaned before use by successive washing with acetone and ultrapure water.

2.2 Instrumentation

Analyses were carried out with a Carbo Erba gas chromatograph (GC), model HRGC 5300, equipped with a 1078 split/splitless injector and flame ionization detector (FID). The injector and detector temperature were set at 190 ^{o}C and 325 ^{o}C respectively. Helium was used as the carrier gas at 5 cm^{3} min^{-1}. The column was a VF-5m 0.25mm x 0.25µm x30m capillary (Lake forst, CA, USA). The temperature program was: initial temperature 175 ^{o}C (hold 2 min), then increase by 10 ^{o}C min^{-1} to 235 ^{o}C (hold 3 min).

2.3 GC calibration

The linear concentration range of the GC-FID measurement of atrazine was tested by duplicate SPME measurements of aqueous standards, with concentrations in the range 0.05 – 50 mg L^{-1} (Figure 1). The detection limit for the detector was 50 pg L^{-1} and the relative standard deviation (%RSD) was 4.2 %, where the detection limit is defined as the concentration of atrazine in the sample which gives rise to a peak with a signal-to-noise ratio (S/N) of 3.

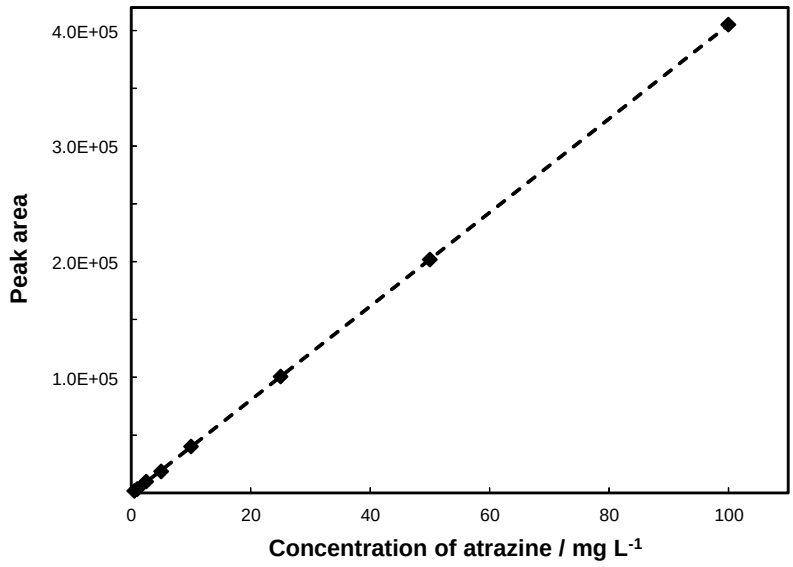

Figure 1: Chromatographic peak area as a function of atrazine concentration in acetone

2.4 Temporal accumulation of atrazine in PDMS and PA solid phases

The solid phase (4 cm length of fiber) was exposed to an aqueous solution (10 mL) of atrazine, 10 mg L^{-1}, at room temperature (19 °C) for a range of accumulation times. Accumulation took place under non-depletive conditions with various rates of magnetic stirring (20, 40, and 60 rpm). The amount of atrazine accumulated in the solid phase was quantified by extraction with 200 μL of acetone, and the extract was injected into the GC. This procedure was repeated twice to ensure complete extraction of the accumulated atrazine. The linear purge was closed during the injection of the extracted analytes in split/splitless injector (2 min delay time).

The solid/water partition coefficients were determined from measurements at partition equilibrium (2 h accumulation time).

3. Results and discussion

3.1 Solid phase/water partition coefficient, K_{sw}

The average values (from 10 measurements) of the solid phase-water partition coefficient measured for atrazine in PDMS and PA are given in Table 1. The higher K_{sw} found for PA as compared to PDMS reflects the greater extent of partitioning of the polar atrazine into the more polar PA polymer phase. Similar values have been reported by others (Valor et al., 2001).

Table 1: Solid-phase/water partition coefficients, K_{sw}, for atrazine at PDMS and PA solid phases

	PDMS	PA
K_{sw}	55	210
SD	3	4
%SD	5.10	1.80

3.2 Temporal accumulation of atrazine in PDMS and PA solid phases

For a non-depletive extraction process, the steady-state accumulation of a single-species target molecule, **X**, in the solid phase as a function of time can be described by an exponential expression (Ai, 1997; Pawliszyn, 1997; Heringa and Hermens, 2003; Benhabib et al., 2008):

$$\bar{c}_{s,\mathbf{X}} = c^*_{w,\mathbf{X}} K_{sw} \left(1 - \exp^{-k_{\mathbf{X}} t}\right) \quad (1)$$

where $\bar{c}_{s,\mathbf{X}}$ is the mean concentration of **X** in the solid polymer phase, $c^*_{w,\mathbf{X}}$ is the concentration of the free **X** species which accumulates in the solid phase, and $k_{\mathbf{X}}$ is the accumulation rate constant. When the rate of accumulation is limited by mass transfer in the aqueous phase, $k_{\mathbf{X}}$ is given by:

$$k_{\mathbf{X}} = \frac{A_s D_{w,\mathbf{X}}}{V_s K_{sw} \delta} \quad (2)$$

where A_s and V_s are the surface area and volume of the solid phase, $D_{w,\mathbf{X}}$ is the aqueous diffusion coefficient of **X**, and δ is the diffusion layer thickness. The magnitude of δ is determined by the hydrodynamic conditions and $D_{w,\mathbf{X}}$.

The temporal profiles for accumulation of atrazine at the PDMS and PA solid phases for a range of solution convection conditions are shown in Figures 2 and 3, respectively. The Figures include the curves computed via Eqs. 1 and 2. The $k_{\mathbf{X}}$ values (derived from plots of $\ln(1 - \bar{c}_{s,\mathbf{X}} / c^*_{w,\mathbf{X}} K_{sw})$ versus time), and the corresponding δ values, determined via Eq. 2, are given in Table 2.

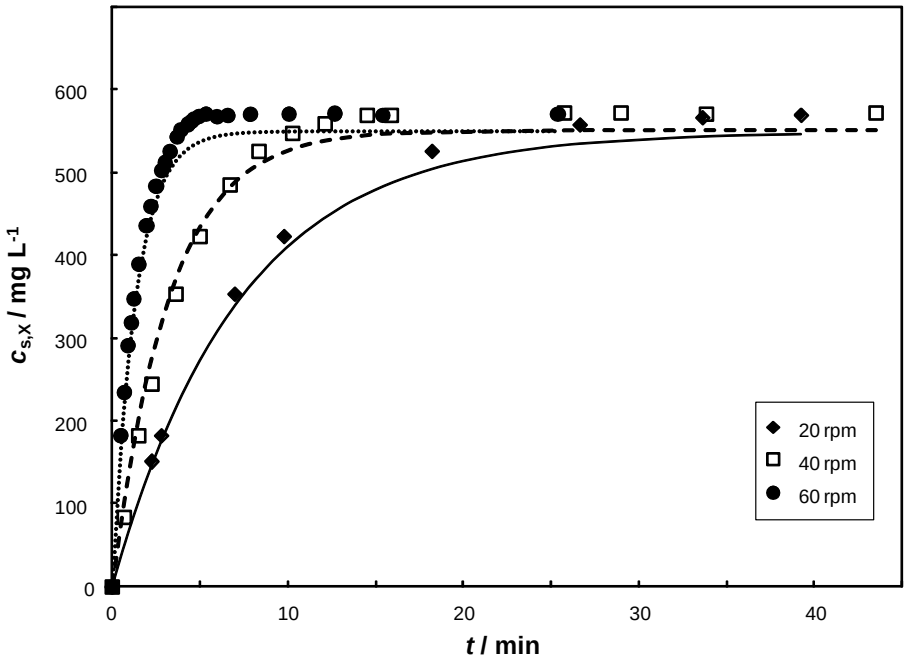

Figure 2: Concentration of atrazine in PDMS solid phase as a function of extraction time, for several rates of solution convection. Points are experimental data; curves are computed from Eqs. 1 and 2

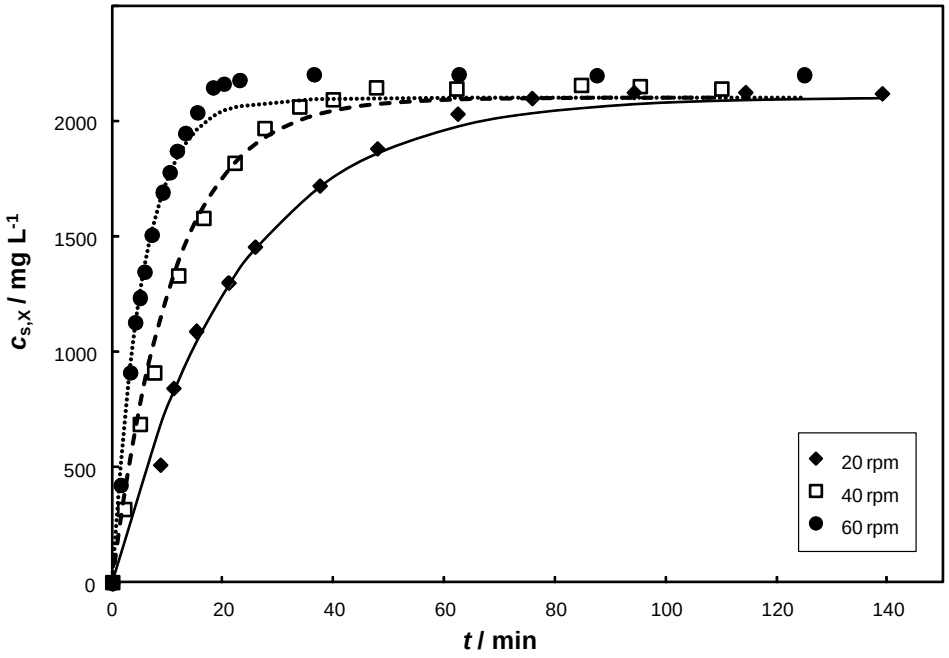

Figure 3: Concentration of atrazine in PA solid phase as a function of extraction time, for several rates of solution convection. Points are experimental data; curves are computed from Eqs. 1 and 2

Table 2: Accumulation rate constant, k_x, and diffusion layer thickness, δ, for atrazine at PDMS and PA solid phases

Rate of stirring / rpm	PDMS		PA	
	k_x / s^{-1}	δ / μm	k_x / s^{-1}	δ / μm
20	2.3×10^{-3}	167	7.5×10^{-4}	134
40	5.2×10^{-3}	74	1.51×10^{-3}	67
60	1.26×10^{-2}	31	3.0×10^{-3}	34

As expected, for a given solid phase the eventual equilibrium concentration of atrazine is independent of the solution convection conditions (Figures 2 and 3). The rate constant for accumulation of atrazine at the PA solid phase is somewhat lower than that at PDMS due to the greater K_{sw} for PA (Eq. 2).
The results in Table 2 show that the partition equilibrium will be attained more rapidly as δ decreases, consistent with the increased diffusive supply flux, J^*_{dif}, of atrazine:

$$J^*_{dif} = D_{w,X} c^*_{w,X} / \delta \quad (3)$$

4. Conclusion

This result confirms that the rate limiting step for accumulation of atrazine in both PDMS and PA is diffusion in the aqueous phase. This feature means that both these solid phases will be useful for studying the speciation dynamics of atrazine in complexing media, i.e. the rate of accumulation will be determined by the lability of the complex species.

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