International Journal of Earth, Energy and Environmental Sciences
ISSN: 2517-942X
Vol:12, No:7, 2018

Speciation Analysis by Solid-Phase Microextraction and Application to Atrazine

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***Abstract*—**The main hypothesis of the dynamics of solid phase microextraction (SPME) is that steady-state mass transfer is respected throughout the SPME extraction process. It considers steady-state diffusion is established in the two phases and fast exchange of the analyte at the solid phase film/water interface. An improved model is proposed in this paper to handle with the situation when the analyte (atrazine) is in contact with colloid suspensions (carboxylate latex in aqueous solution). A mathematical solution is obtained by substituting the diffusion coefficient by the mean of diffusion coefficient between analyte and carboxylate latex, and also thickness layer by the mean thickness in aqueous solution. This solution provides an equation relating the extracted amount of the analyte to the extraction a little more complicated than previous models. It also gives a better description of experimental observations. Moreover, the rate constant of analyte obtained is in satisfactory agreement with that obtained from the initial curve fitting.

***Keywords*—**Pesticide, SPME methods, polyacrylate, steady state.

I. Introduction

THE technique of SPME has found wide application in extraction of organic target compounds from diverse matrices, including environmental compartments, e.g. water [1], soil [2], sediment [3], air [4]. Furthermore, depending on the type of solid phase, the solution convection conditions, 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 [5]-[7].

Analysis of trace organic pollutants in aqueous media involved extraction and preconcentration to determination. Recently, sample preparation by conventional liquid/liquid extraction has been largely replaced by solid-phase extraction (SPE) [8], [9] and later by SPME, as introduced by Pawliszyn and co-workers [10]. The latter is less time consuming and there is no need for using solvents in the extraction. Basic theory for the extraction process and some first applications were published by Pawliszyn et al. [10]. Since then, SPME has been applied to the determination of volatile organic compounds and chlorinated hydrocarbons [11], [12], polyaromatic hydrocarbons (PAH) [13], [16] and pesticides [17]. In connection with that, analytical methods with adequate sensitivity have been developed in recent years, e.g. SPME can determine sub-ppb concentrations [10], [12]. Here, we apply the SPME technique to the analysis of the speciation of atrazine in a dispersion of latex nanoparticles. The atrazine is distributed over its freely dissolved and particle-bound forms. A poly-acrylate (PA) fiber coating is applied as the solid phase for the extraction [14], [15], [18], [19]. The extracted amount as a function of time will form the basis of the interpretation. The latex dispersions are monodisperse, and the particles are spherical with a known radius, meaning that the diffusion coefficient of the bound analyte is known. This will enable us to consider both the extraction kinetics and the eventual extraction equilibrium in computing the dynamic speciation of the analyte.

Using fibers, direct SPME [20] and headspace SPME [21] from aqueous solutions are well described by the relevant theoretical starting equations depicting the multiphase equilibria. In recent years, the utility of the negligible depletion (nd) mode of SPME has been studied by Valor et al. [22] Vaes et al. [23] Heringa and Hermens [24], and Benhabib et al. [25].

In negligible depletion mode, the equilibrium amount of analyte accumulated in the fiber, n_f (mol), is linearly related to the original analyte concentration in the aqueous phase c_w:

$$n_f = K_{fw} V_f c_w \quad (1)$$

where V_f is the volume of the solid phase fiber film, and K_{fw} is the partition coefficient.

The set of starting equations that govern the temporal evolution of c_f towards its equilibrium value $K_{fw} c_w$ has been formulated by Louch et al. [26]. Due to the complexity of the rigorous two-phase transport problem, only numerical solutions were generated. For an unstirred sample solution, the complete extraction process was considered to proceed without any convection, which is not realistic in practice. Under normal conditions, natural convection generally leads to a steady-state transport situation [26] at a certain stage of the accumulation process.

Louch et al. [26] formulated an over simplified treatment of the stirred case by assuming regular agitation such that concentration gradients in the sample solution are negligibly small implying that the condition of flux continuity at the interface is immaterial. Consequently, the ensuing analysis only results in a hypothetical concentration profile inside the polymer phase, which even for these rather unrealistic

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conditions is a mathematically involved expression of Bessel functions [26]. Computation of the accumulated amount as a function of time would require integration of the profile [26], or alternatively, derivation of the concentration gradient at the interface as a function of time.

The most common situation with SPME, however, is that the extraction process is carried out under mild stirring and that the thickness of the steady-state diffusion layer in solution is of the same order of magnitude as the thickness of the polymer coating. In this paper, we develop an approximate analytical model, based on steady-state convective diffusion in the sample solution and continuity of the analyte flux at the fiber/solution interface. The model results in an analytical expression for the time evolution of the accumulated amount of analyte "n_f". For a given accumulation time, n_f is linearly proportional to the original analyte concentration in the sample. Experimental data for the time course of the extraction of atrazine by PA are used in the validation of this approach.

II. Experimental Section

A. Chemicals, Solid Phase Film and Solvent

Atrazine (purity > 97%), was obtained from VWR international (France). Carboxylated latex nanospheres were obtained from Bangs Labs (Fishers, IN) and had a mean diameter 115 ± 2 nm. They are hard spheres with a high density of surface carboxylate groups. The nanospheres were cleaned to eliminate residual surfactant using a mixed bed resin method [15]. Dynamic light scattering (DLS), measured a diffusion coefficient of 4.3 ± (0.2) $x10^{-12}$ m^2/s, in good agreement with the reported diameter given by the manufacturer. Glass fibers with a core diameter of 110 µm and comprised a silica core of radius 55 µm coated with PA (polymer thickness 30 µm) were obtained from Poly Micro Industries (Phoenix, AZ).

The nitric acid, acetone, Sodium chloride, hydroxyd sodium and methanol were purchased from Labbox, (France). The ultra-pure deionized water (R≥ 18 MΩ) was prepared by a Millipore water purification system, equipped with an organic-free kit (Millipore Waters, France).

B. Analytical Procedure

1. SPME Procedure

The PA fibers were cut into pieces (4 cm length of fiber) and cleaned with acetone. Each SPME fiber was exposed to the sample containing 10 mL Millipore water that was spiked with atrazine dissolved in acetone (5 g L^{-1}) to give final concentrations of 10 mg L^{-1} atrazine, and latex spiked from standard with latex dispersion solution ($9.36x10^{-3}$ kg L^{-1}) to give final concentrations $2.12x10^{-3}$ and $9.2x10^{-3}$ kg L^{-1}. The different latex particle concentrations correspond about to 60, and 95 % atrazine binding by the colloid. The matrix solution was adjusted to different pH 2.9, and 5 by concentrated with nitric acid and to pH 9 with hydroxyd sodium (NaOH).

Before extraction, the fibers were exposed during different times under different rate stirring 20, 40 and 60 rpm on a magnetic stirred at 20 ± 2 °C. To measure the free atrazine, the carboxylated latex was separated from analyte by centrifugation (Beckman instruments – Avanti J-25I - USA) about 10 min at 20 000 rpm. To analyse the amount of analyte accumulated by the solid phase film, the fiber was extracted with 200 µL acetone which has an extraction recovery of 100% (RSD 1.0%). This extract was directly injected into a GC system for analysis [7].

2. Extraction Procedure for Determination of Total Atrazine Concentrations: SPE

The supernatant obtained from centrifugation was analysed by SPE. Before extraction, the C18- cartridge was washed with 5 mL methanol and 5 mL Millipore water. Then, volume of sample solution was passed through the cartridge at the maximum flow rate by a vacuum pump.

Subsequently, atrazine retained by the cartridge was eluted with an optimal volume (2 mL) [9] of acetone and dried under reduced pressure for 15 min. The final solution was evaporated to ~ 0.3 mL using a gentle stream of N_2. The extraction recovery obtained with spiked acetone was 99% (RSD 3%). Finally, 20 µL of the eluent was injected into the GC-FID system for atrazine determination.

C. Instrumentation

Analyses of analytes were carried out with a chromatograph (GC), model HRGC 5300, equipped with the flame ionization detector (FID) and a split/splitless injector and. The temperature of injector was 190 °C, and detector temperature was set at 325 °C. Helium was used as the carrier gas at 5 cm^3 min^{-1}. The column was a VF-5m 0.25mm x 0.25µm x 30m capillary. The temperature program was: initial temperature 175 °C (hold 2 min), then increased by 10 °C/min to 235 °C (hold 3 min).

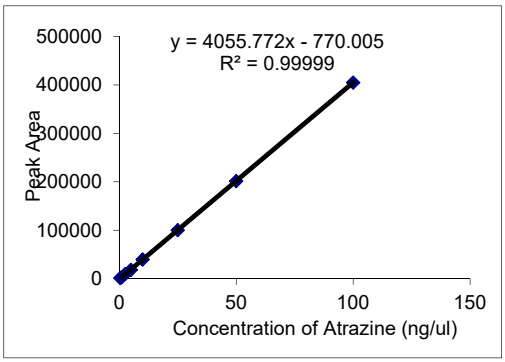

Fig. 1 Chromatographic peak area as a function of atrazine concentration in acetone

D. GC Calibration

The concentration range of the GC-FID measurement of atrazine was tested by extracting aqueous standards in duplicate, with concentrations in the range 0.05 – 50 ng L^{-1} (Fig. 1). The detection limit for the FID detector is equal to 50 pgL^{-1}. We defined the detection limit as ratio between the concentration of atrazine in the sample which gives rise and a

peak with a signal-to-noise ratio (S/N) of 3. Furthermore, we find that the relative standard deviation in our analysis is equal to (%RSD) 4.2% [25].

III. Results and Discussion

A. Temporal Accumulation of Atrazine in PA Solid Phases

We described, by an exponential expression, the steady-state accumulation of a single-species target molecule for a non-depletive extraction process, X, in the solid phase as a function of time [10], [21], [24], [25]:

$$\overline{c_{s,X}} = c^{*}_{w,X} K_{sw} (1 - \exp^{-k_X t}) \quad (2)$$

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

$$k_X = \frac{A_s D_{w,X}}{V_S K_{Sw} \delta} \quad (3)$$

where A_s and V_s are the surface area and volume of the solid phase, $D_{w,X}$ 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 $D_{w,X}$ [25].

As expected, for a given solid phase, the eventual equilibrium concentration of atrazine is independent of the solution convection conditions. Fig 2 shows the different temporal profiles for accumulation of atrazine at the PA solid phases for different percentages of bound colloid. The figures include the curves computed via (2) and (3).

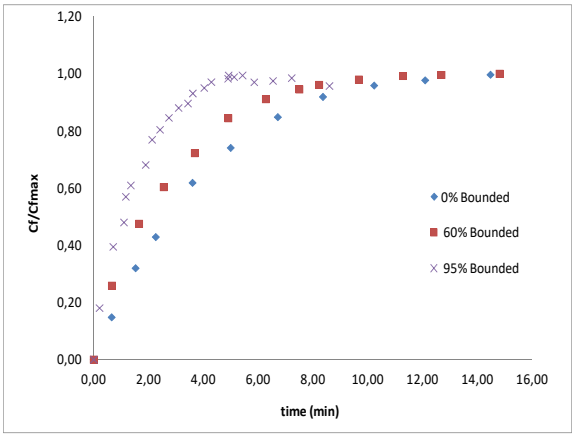

Fig. 2 The concentration of atrazine in the solid phase film as a function of time. PA film was exposed to atrazine bounded at percentage: 0 (♦), 60 (▪), and 95 (×). Symbols represent the experimental data points and the solid line is that computed with model, equation (2)

The k_X values (derived from plots of $\ln(1 - \overline{c_{s,X}} / c^{*}_{w,X} K_{sx})$ versus time), and the corresponding δ values, determined via (3) are given in Table I.

TABLE I
The Average Diffusion Coefficient, the Thicknesses of the Diffusion Layers of the Free Atrazine and the Atrazine Complex in Solution and the Accumulation Rate Constant *k* of Atrazine Calculated by (a) by (3) and (b) Experimentally

% atrazine free	$\overline{D_w}$ ($m^2\ s^{-1}$)	k (s^{-1})^a	k (s^{-1})^b	$\overline{\delta_w}$ (μm)
0	$1x10^{-11}$	$4.1x10^{-2}$	$4x10^{-2} \pm 0.2$	88.5
60	$2x10^{-10}$	$9.8x10^{-3}$	$9.5x10^{-3} \pm 0.4$	189
95	$4x10^{-10}$	$7.8x10^{-3}$	$7.5x10^{-3} \pm 0.3$	206

The results in this table show that δ decreases when the partition equilibrium is attained and the diffusive flux increases. This diffusive, J^{*}_{dif}, of atrazine is given by [19], [25]:

$$J^{*}_{diff} = \frac{D_{w,X} c^{*}_{w,X}}{\delta} \quad (4)$$

This result confirms that the rate limiting step for accumulation of atrazine in 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.

As outlined above, the model assumes an instantaneous establishment of the partition equilibrium at the solid phase/water interface. The model that is developed (expressed by previously (2)) appears to be a good descriptor of the accumulation process.

The coefficients for the correlation coefficient between measured values and the fitted curve all lie between 0.91 and 0.98. The computed curve corresponds to a of *k* value with an ensuing $\overline{\delta_w}$ value.

The latter value was obtained using like describe in [7] by: (a). (3), (b) forced by. (2) and (c) by the plot of $\ln(1 - \frac{\overline{c_s}}{c^{*}_{w} K_{sw}})$ versus time with $D_w = 2.5x10^{-10}$ m^2/s,[26] $A = 2.1x10^{-5}$ m^2/s, $V_s = 2.7x10^{-10}$ m^3 and δ_w K_{sw} are described previously [7], [19] and equal to 210 ± 5 for PA.

Moreover, we observed also in Table I that when the mean of diffusion coefficient decreases, the mean thickness and rate constant increase, this is due to the amount of atrazine bounded in carboxyl latex and it depends on the mean thickness. Furthermore, the rate constant calculated by (2) described previously in [7], [19] and plot of $\ln(1 - \frac{\overline{c_s}}{c^{*}_{w} K_{sw}})$ versus time are in satisfactory agreement with those obtained from the initial curve fitting. The short-time domain of the accumulation profile incorporates the dynamic features of the establishment of a steady-state diffusion situation.

If the particles do not enter the solid phase as it is the case for carboxylate latex, then the partition equilibrium will be

attained for a solid phase analyte concentration prescribed by the free analyte concentration in the sample and the partition coefficient. The particle-bound analyte contributes to the flux but does not participate in the partition. Therefore, the accumulation process is certainly facilitated by the rate of accumulation constant which is also applied in the case of absence of particles.

It may be concluded that nonequilibrium SPME is important to understand the dynamic speciation behavior of atrazine in aqueous solution. Since the rate-limiting step in the extraction of atrazine generally is the diffusion in the aqueous sample solution, the relative enhancement of the accumulation flux in the presence of sorbing nanoparticles is indicative of labile nanoparticles-bound atrazine species, which do not enter the solid phase. The predicted values of the mean thicknesses for colloidal complexes of atrazine in carboxyl modified latex dispersions and their on colloid concentration are in good agreement with experimental data.

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