ELSEVIER

Journal of Chromatography A, 816 (1998) 159–167

JOURNAL OF CHROMATOGRAPHY A

Solid-phase microextraction for determining the binding state of organic pollutants in contaminated water rich in humic organic matter

Jürgen Pörschmann[a,*], Frank-Dieter Kopinke[a], Janusz Pawliszyn[b]

[a]*Centre for Environmental Research, Permoserstrasse 15, 04318 Leipzig, Germany*

[b]*University of Waterloo Department of Chemistry, Waterloo, Ontario, N2L 3G1 Canada*

Received 9 December 1997; received in revised form 11 March 1998; accepted 15 June 1998

Abstract

Solid-phase microextraction (SPME) in both conventional and headspace mode was used for determining the freely available and reversibly bound fraction of phenols and polycyclic aromatic hydrocarbons in contaminated water rich in dissolved polymeric organic matter (DOM). The SPME results obtained by using internal calibration with deuterated surrogates gave the total analyte concentration based on the identical partitioning behaviour of both, native pollutants and deuterated spikes, and agreed well with data from exhaustive LLE. Data obtained with direct and headspace SPME are very similar. Investigated matrices include both contaminated water and artificial DOM solutions. The DOM compounds were isolated from different aquatic and terrestrial sources and cover a wide range of hydrophobicity. A new approach based on progressive dilution of samples rich in DOM was developed for determining both the freely-dissolved fraction of an unknown analyte and its partition coefficients. Theoretical considerations provide strong evidence that the commonly used term 'concentration' in SPME analysis should be replaced by the more appropriate term 'activity' of the solute.

Keywords: Water analysis; Extraction methods; Environmental analysis

1. Introduction

Analysts working in environmental chemistry and biotechnology often need to measure trace chemicals in polluted aqueous samples that are difficult to process. Common methods for analysing aqueous samples include liquid–liquid extraction (LLE) and solid-phase extraction (SPE), both of which fail more or less when applied to highly polluted samples. In this paper the phrase 'highly polluted samples' refers to those rich in dissolved organic polymers, which have properties similar to humic-like materials. Our specific environmental samples are from coal wastewater deposited in an open pond with a volume of about 2 000 000 m^3. The dark brown-coloured water has a high dissolved organic matter (DOM) concentration (more than 350 $mg\,l^{-1}$), the fulvic acid fraction accounts for about two thirds and the more hydrophobic humic acids for about one third [1]. DOM is known to interact with dissolved organic pollutants (see most recent contribution [2] and refs. cited therein). In environmental

*Corresponding author.

0021-9673/98/$19.00
PII: S0021-9673(98)00525-1

science and other fields (especially pharmacology), several properties and effects of organic chemicals such as transport behaviour, bioavailability and toxicity are heavily dependent on the freely-available concentration. Therefore, it can be necessary to distinguish between the total and the freely-dissolved fraction of pollutants, both present in the water phase.

Solid-phase microextraction (SPME) has become an established method for solvent-free extraction of analytes in recent years. Special methodological approaches such as headspace and derivatization SPME, are appropriate for analysing organic compounds covering a wide range of volatility and polarity [3,4]. Although SPME was originally designed to solve analytical problems in conjunction with a hot GC injector, the method could potentially be used for solving physicochemical problems [5] or — in conjunction with HPLC [6], UV spectroscopy [7], electrophoresis [8], electrochemistry [9], etc. — to extend the range of compounds which may be investigated and to investigate speciation phenomena.

The application of SPME to contaminated waters rich in DOM has recently been described by us [10]. It became evident, that an external calibration gives the freely-dissolved fraction of a solute, whereas internal calibration using deuterated surrogates gives the total concentration. The objectives of the present paper are:

(i) To investigate the usefulness of both direct and headspace SPME to draw conclusions on the binding states of low-molecular-mass pollutants including phenols and polycyclic aromatic hydrocarbons (PAHs) and to determine the validity of the concept for both weakly and strongly hydrophobic solutes.

(ii) To determine both the total concentration and the partition coefficients on DOM of hydrophobic sorbates, where no deuterated surrogate is available and partition coefficients are also unknown.

(iii) To detail the relationships between analyte concentration and analyte activity measured by SPME.

(iv) To investigate the sorption potential of DOMs of various origins towards PAHs having a wide range of hydrophobicity.

2. Experimental

2.1. Isolation of humic organic material

Humic and fulvic acids (HA and FA, respectively) were isolated from the coal wastewater by the method detailed in [11]. The humic acids from the sediment on the bottom of the pond were isolated by an extraction with 1 *M* NaOH without using XAD resins, according to the guidelines of the International Humic Substances Society (IHSS) [12]. In the framework of this paper, four polymers were investigated: HA and FA isolated from coal wastewater (A-HA and A-FA, respectively; A stands for the anthropogenic origin), a HA isolated from associated coal wastewater sediment on the bottom of the coal wastewater pond (T-HA; T stands for a terrestrial source), and a FA isolated from a water plant located in Fuhrberg near Hannover (AQ-FA; AQ stands for a groundwater aquifer). The carbon content in the isolated DOM determined by microanalysis was as follows (sum of sulphur and nitrogen is given in parenthesis): A-HA 47.1% (13.9%), A-FA 39.4% (12.2%), T-HA 50.0 (11.4%), AQ-FA 47.2% (2.1%). Some structural features of these isolated HOMs are detailed in [13].

2.2. Materials and methods

2.2.1. Standard mixtures

Standard mixtures of unlabelled and perdeuterated phenols and PAHs from naphthalene to chrysene (>99% purity) were all obtained from Promochem (Wesel, Germany) or Supelco (Munich, Germany). Analytical reagent grade solvents were purchased from Merck (Darmstadt, Germany).

The SPME syringe and PDMS fibres with a coating thickness of 7 μm were purchased from Supelco. The fibres were conditioned at 270°C under helium overnight prior to use.

2.2.2. LLE

All glassware used for shaking or extraction procedures were thoroughly washed and silanized prior to use. Sodium azide (0.05%, w/w) was added to the original coal wastewater (and to the artificial DOM solutions, see below) as an inhibitor of micro-

bial activity. The original coal wastewater was diluted 1:1 with deionised water prior to extraction, in order to lower the tendency to form emulsions. The organic solvent was spiked with deuterated internal standards to give concentrations of 10 ppm of phenols ([$^2H_5$]phenol, [$^2H_7$]*o*-cresol, [$^2H_3$]2,4-dimethylphenol) and 10 ppb of PAHs (from [$^2H_8$]naphthalene through [$^2H_{12}$]chrysene). The LLE was done by vigorously shaking 25 ml of diluted coal wastewater with 25 ml of solvent for 30 min in a 50-ml vial (no headspace to avoid losses). The organic extracts were dried and concentrated by rotary evaporation under nitrogen at 40–60°C, depending on the solvent, down to a final volume of 200 μl. Further solvent reduction to improve detection limits was not performed due to significant losses of target analytes.

2.2.3. SPME to investigate coal wastewater

For conventional SPME, 40-ml amber vials were completely filled (to avoid significant headspace losses occurring with analytes having high Henry coefficients) with the undiluted coal wastewater and agitated with a laboratory-made stir bar made of glass at 800 rpm. The stir bar was silanized prior to use in order to avoid adsorption of hydrophobic analytes as was observed with PTFE-made stir bars in previous experiments. For headspace SPME, 25 ml of the undiluted aqueous samples were placed in 40-ml amber vials capped with PTFE-coated septa (Supelco, Munich). Fibres were desorbed in the splitless mode of the GC injector. SPME internal calibration was performed by spiking the wastewater with deuterated phenols and PAHs (internal standards) to give concentrations of 10 ppm and 10 ppb, respectively. Target analyte concentrations were calculated from signal ratios at the specific ion trace: e.g. signal intensity of $m/z=128$ divided by signal $m/z=136$ for naphthalene and deuterated naphthalene, respectively, and so forth. SPME external calibration was performed using deionised water with known concentrations of phenols (1–50 ppm) and PAHs (0.5–25 ppb). The calibration was found to be linear in this range. In all cases, the SPME sampling time was sufficient to ensure equilibrium conditions (overnight procedure). When working with internal standards, the SPME need not be in equilibrium, because signal ratios are determined rather than absolute peak areas. In this case, the sampling time was determined by the rate of sorption and desorption steps on DOM, which turned out to be fast [10].

2.2.4. SPME to investigate artificial DOM solutions

External calibration was done by spiking pure deionised water with deuterated PAHs to give concentrations of 10 ppb each. Then the four artificial DOM solutions to be analysed (see above), each having a DOM concentration of 100 ppm, were also spiked with 10 ppb of deuterated PAHs. SPME was performed for 15 h as stated above. The experiments were repeated with a DOM concentration of 200 ppm. Finally, a PAH concentration of 2 ppb was applied to investigate both 100 ppm and 200 ppm DOM solutions; i.e. for each PAH four data sets were obtained, which were averaged.

2.2.5. Instruments and apparatus

An HP 5971B GC–MS system and a GCD system (both from Hewlett-Packard, Palo Alto, CA, USA) were used. The capillary columns were 30 m×0.25 mm I.D. with a 0.25 μm stationary phase HP-5 (Hewlett-Packard) or SPB-5 (Supelco). The GC conditions were as follows: $T_{injector}=300$°C (7 μm fibre and injection of solvent extracts); temperature program 40°C for 3 min, 10°C min^{-1} up 290°C held for 15 min. The data acquisition for the HP 5971B device was performed using the SIM mode.

3. Results and discussion

3.1. Liquid–liquid extraction

The addition of deuterated standards for quantification of nondeuterated analytes, a very precise and accurate calibration method, is crucial in the case of LLE of solutions rich in HOM. Possible methods of calibration include spiking the wastewater prior to extraction, spiking the organic extract, or spiking the organic solvent prior to extraction. Spiking the solvent prior to extraction proved to be the optimal quantification method, since the standards are sub-

jected to the same losses as the target analytes and a significant removal of standards by the HOM is less likely.

The ratio of solvent to diluted wastewater was 1:1, in order to diminish the effects of emulsion formation. Table 1 gives the results of wastewater extractions using toluene, chloroform and methylisobutyl ketone (MIBK). The results indicate that the ketone possesses the highest extraction efficiency for phenols, which can be attributed to its relatively high polarity (dipole moment: 2.7 D [14]) and its capability to enter into hydrogen bonding. The combined extracts of three consecutive extractions with either toluene and chloroform give almost identical recoveries compared with a single extraction using MIBK. For PAHs, the three solvents yield identical recoveries, as can be expected.

The data for PAHs given in Table 1 are independent of the pH values of the aqueous phase (pH 2–13). Obviously, the portion of pollutants accessible to LLE does not significantly depend on the conformation of the DOM, i.e. coiled or stretched-out.

3.2. Conventional SPME to determine total and free concentrations of sorbates

The aim of applying solvent-free SPME to the analysis of coal wastewater is both to replace the LLE and to achieve more information about the binding state of pollutants. In principle, the extraction phenomena are similar in LLE and SPME, but the volume of the extracting phase is very different. Therefore, due to the low fibre volume (e.g. $2.57 \cdot 10^{-5}$ ml in the case of a 7 μm PDMS fibre), SPME can be applied such that equilibria in the sample solution are not significantly disturbed [10], whereas LLE tends to shift phase equilibria completely towards the extraction phase.

In SPME literature, the solute concentration is thought to be measured, but in fact, its activity is measured. The significance of this becomes evident when performing SPME in an aqueous solution containing another solvent, e.g. methanol (1% or so). Although the analyte concentrations may be identical, the fibre uptake of the given analyte will be significantly lower in the methanol-modified solution. In the latter case, the entropic term, which describes the incompatibility of solvent and hydrophobic analyte, becomes smaller. Analogously, SPME measures the activity of target analytes in solutions containing DOM. In the present paper we treat the macromolecular DOM as a separate, colloidal phase. The decrease of analyte activity in the presence of DOM is attributed to a partitioning of the analyte between these two phases, the water phase and the DOM phase. Because the SPME is calibrated with aqueous solutions of known analyte concentrations, the measured analyte activity in the water phase gives the analyte concentration directly. This, however, holds only as far as the activity coefficients of the analyte are identical in the standard sample and the unknown sample.

The SPME results for phenols and PAHs in the

Table 1
Liquid–liquid extraction of coal wastewater with solvents of different polarity[a]

Sorbate	Solvent		
	Toluene	Chloroform	Methylisobutyl ketone
Phenol	87.6	83.5	101
o-Cresol	5.6	5.8	6.5
m/*p*-Cresol	31.1	30.0	35.2
3,4-Dimethylphenol	1.6	1.5	2.0
Naphthalene	25.2	24.7	24.0
Fluorene	7.6	7.3	7.7
Phenanthrene	12.2	11.8	12.0
Anthracene	3.4	3.4	3.5
Fluoranthene	4.9	4.6	4.8
Pyrene	5.2	5.0	5.5

[a] Data given as ppm for phenols and as ppb for PAHs; data are average of three replicates, R.S.D. = 5–9%.

coal wastewater by using both external and internal calibration are given in Table 2. The higher the hydrophobicity of the PAHs, which can be expressed by their octanol–water partition coefficient K_{OW} [15], the higher the differences between the 'external' SPME and the LLE data (cf. Table 1). Clearly, these differences are equal to that very portion which is reversibly bound to the DOM, because SPME detects only the freely-available analytes. In contrast, data obtained by internal calibration coincide quite well with LLE data. These findings are theoretically clarified in [10]. Briefly, partition coefficients can be calculated using SPME data based on both external and internal calibration ($c_{SPME,\ external}$ and $c_{SPME,\ internal}$):

$$K_{DOM,i} = \frac{c_{bound,i}}{c_{free,i}} \times \frac{1}{c_{DOM}} = \frac{c_{total,i} - c_{free,i}}{c_{free,i}} \times \frac{1}{c_{DOM}} = \frac{c_{SPME,internal,i} - c_{SPME,external,i}}{c_{SPME,external,i}} \times \frac{1}{c_{DOM}} \quad (1)$$

where $c_{free,i}$, $c_{bound,i}$ and $c_{total,i}$ are the concentrations of the analyte i in the freely-dissolved state, reversibly bound on the DOM phase and in total, respectively, all in relation to the amount of water in the sample. $K_{DOM,i}$ is the partition coefficient for the analyte i between DOM and water and c_{DOM} is the concentration of DOM in the sample (mg l^{-1}).

According to DOC measurements of the wastewater (DOC = 385 mg l^{-1}) and the consideration of low-molecular-mass compounds ($M_r < 500$) having an organic carbon concentration of about 110 mg l^{-1} as being of minor importance as sorbents, the DOM is supposed to be $c_{DOM} \approx 610$ mg l^{-1} (assuming an averaged organic carbon content of 45% of the DOM). This concentration is higher than that obtained according to the isolation procedure for humic-like substances as given above (350 mg l^{-1}) and therefore also comprises fractions not accessible to the operationally defined preparation scheme for humic substances. These fractions are presumed to be mainly responsible for the fibre fouling.

Partition coefficients given in Table 2 are obtained on the basis of relationship Eq. (1). For the PAHs fluorene, anthracene and pyrene, where deuterated standards for internal calibration were available, these data were in good agreement with results from previous investigations using DOM of the same type (Table 2, 5th column). For the more hydrophilic sorbates, including phenols and naphthalene, the differences between the total and the free concentrations are within the scattering of the experimental data, such that reliable partition coefficients cannot be calculated.

To generalise these findings for analytical purposes we conclude that:

Table 2
Analyte concentrations in the coal wastewater obtained by SPME using external and internal calibration

Sorbate	Method				
	SPME		log K_{DOM}		Headspace SPME
	External calibration	Internal calibration	Calculated according to Eq. (1)	From literature see [10]	External calibration
Phenol	97.0	94.0	[b]	0.88	104.5
o-Cresol	6.2	6.0	[b]	1.35	7.1
m/*p*-Cresol	35.6	[c]	[b]	1.35	38.1
Naphthalene	21.6	27.5	[b]	2.79	25.8
Fluorene	3.4	7.3	3.28	3.58	3.6
Phenanthrene	2.1	[c]	[c]	3.98	2.2
Anthracene	0.55	3.5	3.94	4.11	0.6
Fluoranthene	0.40	[c]	[c]	4.44	[d]
Pyrene	0.35	4.9	4.34	4.53	[d]

[a] Data given as ppm for phenols and as ppb for PAHs; data are average of three replicates, R.S.D. = 4–13%.
[b] Degree of sorption is too low to be measured by SPME.
[c] Deuterated standard for internal calibration was not available.
[d] Not detected by headspace SPME.

(i) SPME based on external calibration and LLE give almost identical results for analytes with low to medium hydrophobicity (log $K_{OW}<3.0$), even in solutions with a DOM content of some 100 mg l^{-1}. Among these analytes are phenol (log $K_{OW}=1.49$), cresols (log $K_{OW}=1.94$) and naphthalene (log $K_{OW}=3.30$) (data from [16–18]).

(ii) For more hydrophobic analytes, internal calibration of SPME by means of deuterated surrogates is recommended to determine total concentrations. If the deuterated surrogates are not available, then the free concentration $c_{free,i}$ of the analyte (measured by external calibration) has to be corrected by the sorption term in Eq. (1) $(1+K_{DOM}\ m_{DOM}/m_{water})$ in order to calculate its total concentration $c_{total,i}$, either by using a similar deuterated surrogate (e.g. deuterated pyrene if deuterated fluoranthene is not available) or by approximating the sorption term based on one of the known relationships between K_{DOM} and K_{OW} [15], e.g. $K_{DOM}\approx 0.25\ K_{OW}$.

The presented findings and the theoretical background are helpful to explain some peculiarities which have been reported in the special literature: For example, it was found that SPME with external calibration and LLE yield comparable results for the nerve agents sarin and tabun in sewage waters possessing humic-like material, whereas the nerve agent VX shows a poorer SPME recovery than that of LLE [19]. When comparing the K_{OW} values given in [14], sarin ($C_4H_{10}FO_2P$; log $K_{OW}=0.24$) and tabun ($C_5H_{11}N_2O_2P$; log $K_{OW}=-1.44$) can be expected to enter very little into hydrophobic interactions with DOM, whereas VX ($C_{11}H_{26}NO_2PS$; log $K_{OW}=2.04$) may undergo more hydrophobic interactions with DOM. Specific interactions of VX with DOM also have to be considered in addition to the hydrophobic partitioning.

3.3. Headspace SPME to determine total and free concentrations of sorbates

As discussed above, the SPME fibre needs to be protected from direct contact with the DOM in some cases. Two approaches have been taken to minimise matrix interferences: enclosing the fibre in a hollow fibre membrane [20], and extracting the analytes from the headspace above the sample solution [21,22]. Headspace SPME [20–22] is a good supplement to conventional SPME when analysing volatile compounds in 'corrosive' or dirty samples, among them strong alkaline or acidic solutions or solutions with high salinity [23] that otherwise would readily degrade the fibre coating. In the framework of this paper we tested the usefulness and limitation of this approach to determine the binding state of pollutants in solutions rich in DOM. From the methodological point of view the headspace approach might be more beneficial than the conventional SPME, because a possible fibre fouling attributed to DOM adsorption can be excluded a priori. In our experience, attention should be paid to the establishment of the equilibrium between the aqueous phase and the headspace, especially when investigating less volatile analytes and solutions with high salinity [23,24]. Mass transfer rates through boundary layers may be considerably reduced in saline solutions compared with pure water. For thermodynamic reasons, the fibre uptake by conventional (solution) and by headspace SPME has to be identical under equilibrium conditions, provided that the sampling is exclusively determined by a partition process rather than by surface adsorption on the fibre. This was confirmed at least for PAHs (two to four rings) by a series of measurements [25].

Table 2 (last column) lists freely-dissolved concentrations of target phenols and PAHs measured by headspace SPME with external calibration. The good agreement with data obtained from conventional SPME (2nd column) is striking. However, tracing sorption phenomena using headspace SPME is restricted to analytes with medium Henry coefficients. For analytes with very low Henry coefficients such as PAHs with more than three rings (e.g. $H_{pyrene}=0.0012$ kPa m^3/mol) [26], the equilibration time at 23°C is unreasonably long (>16 h). One way to accelerate the equilibration, i.e. to enhance analyte evaporation rates and mass transfer at the water–gas interface [27], is to increase the sample temperature. A temperature of 50°C proved to be sufficient even for four-ring PAHs. Elevated temperatures, however, can shift sorption equilibria further away from typical environmental conditions. Another method is to preequilibrate the aqueous phase with its headspace. Fig. 1 gives the time profiles for [$^2H_{12}$]chrysene (1 ppb) at 50°C in pure water, a humic and a fulvic acid solution (100 ppm T-HA and

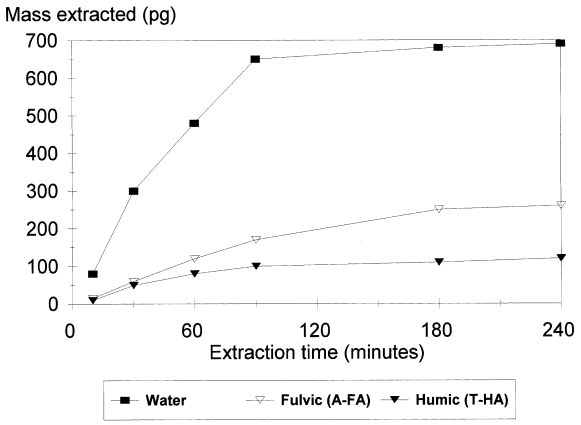

Fig. 1. Time profile for headspace SPME of 1 ppb [$^2H_{12}$]chrysene at 50°C (c_{DOM} = 100 ppm).

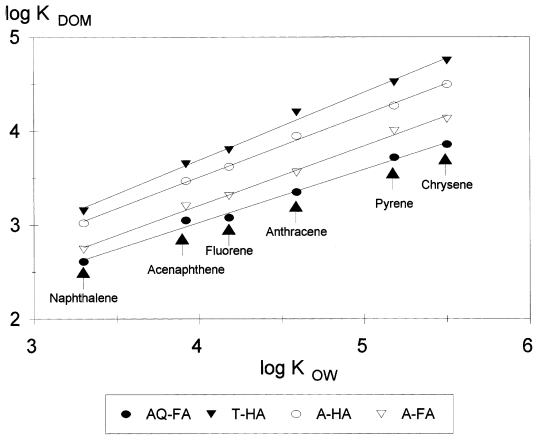

Fig. 2. Log K_{DOM} vs. log K_{OW} for PAHs in DOM of various origins.

A-FA, respectively). Prior to extraction, each sample had been allowed to equilibrate with its headspace overnight. The relatively fast establishment of SPME-extraction equilibrium (within a period of 90–180 min) and the higher sorption capability (i.e. smaller fibre uptake) of the HA compared with that of the FA are evident.

Another limitation of headspace SPME occurs with compounds possessing very high Henry coefficients such as alkanes (e.g. $H_{dodecane}$ = 750 kPa m^3/mol) [26], which are completely expelled from the aqueous phase. Therefore, the effect of DOM on the fibre uptake is neglected.

3.4. Calculation of PAH partition coefficients on DOM of various origins

Fig. 2 details the sorption behaviour of DOM of various origins towards naphthalene through chrysene. The partition coefficients K_{DOM} were calculated according to Eq. (1). The strong correlation of log K_{DOM} versus log K_{OW} ($r^2 > 0.96$ in all cases) indicates the dominance of nonspecific, hydrophobic interactions in the sorption of PAHs. As shown by Fig. 2, there is a clear ranking in sorption capability: the highest partition coefficients were measured for the hydrophobic HA isolated from sediment, followed by the aquatic HA and FA both isolated from the coal wastewater. The FA isolated from the groundwater has the lowest sorption potential.

According to the concept developed in [15] sorption coefficients can be used to calculate the solubility parameters, δ, of the sorbents. They can be considered as a measure of polarity of the dissolved polymer. On the basis of the sorption data in Fig. 2 we calculated the following δ values: $\delta_{AQ\text{-}FA} = 12.85 \pm 0.4$, $\delta_{A\text{-}FA} = 12.50 \pm 0.35$, $\delta_{A\text{-}HA} = 11.85 \pm 0.55$, $\delta_{T\text{-}HA} = 11.30 \pm 0.7$ $(\text{cal cm}^{-3})^{0.5}$ (1 cal = 4.184 J). They are close to the value of 12.5 ± 1.0, which was given in [15] as characteristic of humic substances. The sequence reflects a decreasing polarity of the humic substances from the aquatic fulvic acid up to the terrestrial humic acid. The least polar humic substance (T-HA) is the best sorbent for the hydrophobic sorbates. The range of scattering in the δ values results from the different PAHs (naphthalene through pyrene) which were used as probe molecules.

3.5. Calculation of partition coefficients by means of successive sample dilution

In the case of complete reversibility of the sorption onto DOM, partition coefficients K_{DOM} can be calculated from Eq. (2), which is obtained by rearranging Eq. (1):

$$\frac{1}{c_{free}} = \frac{1}{c_{total}} + \frac{K_{DOM}}{c_{total}} \cdot c_{DOM} \quad (2)$$

Plotting $1/c_{free}$ (measured by SPME) vs. c_{DOM}

gives a slope related to K_{DOM}. The total concentration of the analyte in the original, undiluted sample ($c_{total,0}$), is reduced via dilution by a factor of $1/(1+D)$, where D is the ratio of dilution (e.g. $D=1$ for a 1:1 dilution). Introduction of the dilution ratio into Eq. (2) gives:

$$\frac{1}{c_{free}} = \left[\frac{1}{c_{total}} + \frac{K_{DOM} c_{DOM,0}}{c_{total,0}} \right] + \frac{D}{c_{total,0}} \qquad (3)$$

Plotting $1/c_{free}$ vs. D gives the slope $1/c_{total,0}$. K_{DOM} can be calculated from the interception with the y-axis. To illustrate this procedure, Fig. 3 shows plots $1/c_{free}$ vs. D for fluorene, phenanthrene, fluoranthene and pyrene. The resulting data (calculated on the basis of Eq. (3)) are given in Table 3. For $c_{DOM,0}$ a value of 610 mg l^{-1} was used, as mentioned in Section 3.2.

The LLE data (Table 1) and the data obtained by SPME with internal calibration (Table 2) correlate reasonably well with the concentrations given in Table 3. Therefore, the assumption that all analyte molecules are accessible to reversible partitioning proved to be correct. For sorbates with only little hydrophobic partitioning such as phenols, SPME is not appropriate to measure sorption coefficients. The reason is that the sorbed fraction is determined indirectly, i.e. as the difference between the total and the freely-dissolved fraction.

If the analyte to be investigated is not available as a pure reference substance, SPME cannot be simply calibrated. Nevertheless, sorption coefficients can be

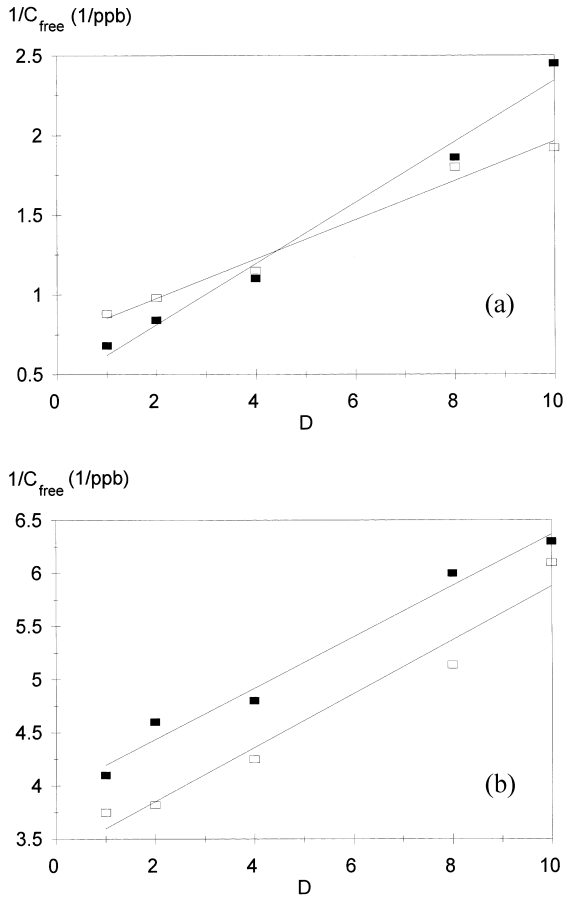

Fig. 3. Reciprocal free concentrations measured by SPME against the dilution ratio (D) of the coal wastewater; (a) ■, fluorene; □, phenanthrene; (b) ■, pyrene; □, fluoranthene.

Table 3
Calculation of total sorbate concentrations and partition coefficients by SPME using progressive dilution of the wastewater

Sorbate	$c_{total,0}$ (ppb)	log K_{DOM}	Linear regression according to Eq. (3)
Naphthalene	23.5	2.66	$y=0.043x+0.055$ $r=0.971$
Fluorene	6.5	3.60	$y=0.154x+0.532$ $r=0.983$
Phenanthrene	8.2	3.91	$y=0.123x+0.730$ $r=0.976$
Fluoranthene	3.9	4.30	$y=0.256x+3.410$ $r=0.970$
Pyrene	4.3	4.40	$y=0.242x+3.951$ $r=0.965$

determined by means of the method of successive dilution, according to Eq. (4), which follows from Eq. (3):

$$\frac{n_0}{n_D} = 1 + \frac{D}{1 + K_{\mathrm{DOM}} c_{\mathrm{DOM},0}} \quad (4)$$

n_0 and n_{D} are the signal intensities of SPME analysis (in arbitrary units) for samples with the dilution ratios zero and D, respectively, and $c_{\mathrm{DOM},0}$ is the concentration of DOM in the undiluted sample. The advantage of the presented method of successive dilution is obvious: the only information necessary for determination of sorption coefficients is the concentration of DOM in the original sample. All the other data come from SPME analyses of a dilution series.

Acknowledgements

The authors thank Mrs. M. Hoyer, U. Bachmann and C. Maier for their excellent technical assistance.

References

[1] J. Pörschmann, U. Stottmeister, Chromatographia 36 (1993) 207.
[2] Y.-P. Chin, G.R. Aiken, K.M. Danielsen, Environ. Sci. Technol. 31 (1997) 1630.
[3] Zh. Zhang, M. Yang, J. Pawliszyn, Anal. Chem. 66 (1994) 844A–853A.
[4] L. Pan, J. Pawliszyn, Anal. Chem. 69 (1997) 196.
[5] Zh. Zhang, J. Pawliszyn, J. Phys. Chem. 100 (1996) 17648.
[6] A.A. Boyd-Boland, J. Pawliszyn, Anal. Chem. 68 (1996) 1521.
[7] B.L. Wittkamp, S.B. Hawthorne, D.C. Tilotta, Anal. Chem. 69 (1997) 1197.
[8] A.-L. Nguyen, J.H.T. Luong, Anal. Chem. 69 (1997) 1726.
[9] F. Guo, T. Gorecki, D. Irish, J. Pawliszyn, Anal. Commun. 33 (1996) 361.
[10] J. Poerschmann, Zh. Zhang, F.D. Kopinke, J. Pawliszyn, Anal. Chem. 69 (1997) 597.
[11] K. Wienhold, G. Hanschmann, Chem. Techn. 43 (1991) 232.
[12] C.E. Clapp, M.H.B. Hayes, in: C.E. Clapp, M.H.B. Hayes, N. Senesi, S.M. Griffith (Editors), Humic Substances and Organic Matter in Soil and Water Environments, International Humic Substance Society, St. Paul, MN, 1996, Section 1, p. 3.
[13] J. Pörschmann, F.-D. Kopinke, M. Remmler, K. Mackenzie, W. Geyer, S. Mothes, J. Chromatogr. A 750 (1996) 287.
[14] Daylight Chemical Information Systems, Daylight Software, CLOGP-4.34, Irvine, CA, 1994.
[15] F.D. Kopinke, J. Poerschmann, U. Stottmeister, Environ. Sci. Technol. 29 (1995) 941.
[16] A.F.M. Barton, Chem. Rev. 75 (1975) 731.
[17] B.J. Herbert, J.G. Dorsey, Anal. Chem. 67 (1995) 744.
[18] M.J. Kamlet, R.M. Doherty, M.H. Abraham, Y. Marcus, R.W. Taft, J. Phys. Chem. 92 (1988) 5244.
[19] H.-A. Lakso, W.F. Ng, Anal. Chem. 69 (1997) 1866.
[20] T. Nilsson, F. Pelusio, L. Montanarella, B. Larsen, S. Facchetti, J.O. Madsen, J. High Resolut. Chromatogr. 18 (1995) 617–625.
[21] Zh. Zhang, J. Pawliszyn, Anal. Chem. 65 (1993) 1843.
[22] B. Mac Gillivrey, J. Pawliszyn, P. Fowlie, Ch. Sagara, J. Chromatog. Sci. 32 (1994) 317.
[23] K. Buchholz, J. Pawliszyn, Anal. Chem. 66 (1994) 160.
[24] D. Louch, S. Motlagh, J. Pawliszyn, Anal. Chem. 64 (1992) 1187.
[25] A. Georgi, Dissertation, University of Leipzig, 1997.
[26] D. Mackay, W.Y. Shiu, J. Phys. Chem. Ref. Data 10 (1981) 1175.
[27] J. Ai, Anal. Chem. 69 (1997) 3260.