Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1029 (2004) 263–266
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Short communication

Air/polymer distribution coefficients for polycyclic aromatic hydrocarbons by solid-phase microextraction sampling

Kamil Kolář[a,*], Miroslav Ciganek[a,b], Jiří Malecha[a]

[a] *Faculty of Chemistry, Institute of Chemistry and Technology of Environmental Protection, Brno University of Technology, Purkyňova 118, Brno 612 00, Czech Republic*
[b] *Veterinary Research Institute, Hudcova 70, Brno 621 32, Czech Republic*

Received 22 April 2003; received in revised form 7 November 2003; accepted 1 December 2003

Abstract

Two methods to estimate distribution coefficients (*K*) between air and poly(dimethylsiloxane) (PDMS) coating of solid-phase microextraction (SPME) fibers for eight low molecular polycyclic aromatic hydrocarbons (PAHs) there are presented. The PDMS phases were used for determination of the coefficients according to equilibrium theory with help of a developed static calibration system (SCS). Another way to estimate the coefficients is based on the use of a linear relationship between the logarithm of the coefficients (log *K*) and linear temperature–programmed retention indexes (LTPRI) of the compounds without necessity to calibrate. The log *K* values for both of methods ranged from 5.2 (naphthalene) to 8.9 (pyrene) at 22 °C. Relative standard deviation (R.S.D.) of log *K* for each compound determined by static calibration was no more than 5.3%. R.S.D. of retention times for LTPRI indices did not exceed 0.28% for repeated injection. All experiments were implemented on a GC–MS system.

Keywords: Distribution coefficients; Air; Solid-phase microextraction; Polynuclear aromatic hydrocarbons; Poly(dimethylsiloxane)

1. Introduction

Solid-phase microextraction (SPME) is considered to be a simple and cost-effective alternative to the conventional air sampling methods for the analysis of volatile organic compounds (VOC) in environmental air samples [1,2]. In case of polycyclic aromatic hydrocarbons (PAHs), the low vapor pressure [3,4] and the high sorption ability [5,6] complicates preparing of the gaseous standards and the use of the SPME method. Therefore, the SPME applications have been restricted to the identification of PAHs in diesel exhaust [1,7,8] or to measurement in a simple static mode calibration [9] so far.

The determination of distribution coefficients (*K*) between the polymer SPME phase and the gaseous matrix is usually a crucial step in the sampling of any airborne compounds by SPME. The most frequently used technique for their determination is the experimental measurement in static [1] or dynamic [10] calibration systems under equilibrium [11] or nonequilibrium [12,13] conditions. In a static equilibrium system, the amounts of analytes partitioned to the coating are directly proportional to their concentrations in the gaseous phase. The *K* values then can be calculated as a simple ratio of equilibrium concentrations of the extracted analytes in polymer and gas phases (when $V_g \gg KV_f$, where V_g and V_f are the gas sample and the SPME fiber volumes).

Another way to estimate the distribution coefficients exploits a linear relationship between the logarithm of *K* (air/poly(dimethylsiloxane); PDMS SPME) of the analytes and their indexes from the linear temperature–programmed capillary gas chromatography [14]. This relationship (usually determined by the homologous series of *n*-alkanes) can by applied to the determination of log *K* values of unknown compounds whose LTPRI indices were determined by the separation under the same chromatographic conditions as the series of *n*-alkanes [15].

The previous study [16] showed that sensitivity of the 100 μm PDMS phases to extraction of the PAHs from gaseous matrixes were greater than the 75 μm carboxen phases. The purpose of this study was the determination

* Corresponding author.
E-mail address: kolar@fch.vutbr.cz (K. Kolář).

0021-9673/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2003.12.007

of the distribution coefficients by both described methods and the comparison of the values obtained. The established distribution coefficients were used for approximate quantification of low molecular weight PAHs in both indoor and outdoor air samples.

2. Experimental

2.1. Chemicals, instruments, and supplies

Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, and biphenyl standards (purity of 99%), isooctane and dichloromethane for the standard stock solution preparation, and SPME devices with 100 μm poly(dimethylsiloxane) coated fiber assemblies, were obtained from Supelco (Bellafonte, PA, USA), respectively. *n*-Decane, *n*-undecane, *n*-dodecane, *n*-tridecane, *n*-tetradecane, *n*-pentadecane, *n*-hexadecane, *n*-heptadecane, *n*-octadecane, *n*-nonandecane, and *n*-eicosane (Sigma-Aldrich, St. Louis, MO, USA) for determination of LTPRI indexes and distribution coefficients of *n*-alkanes were used.

The GC/MS system used for all experiments consisted of Fisons GC8000 gas chromatograph equipped with Fisons mass spectrometr TRIO 1000 (Fisons Instruments, Manchester, England). The analytes were separated on a capillary column (30 m, 0.25 mm i.d., 0.25 μm—DB-5 ITDMS stationary phase; J & W Scientific, Folsom, CA, USA). The mass spectrometer was operated in the EI+ mode (E = 70 eV, full scan mode from 40 to 300 amu). The transfer line was held on 250 °C, source temperature was 200 °C, scan time 0.19 s.

2.2. Determination of distribution coefficients of PAHs by static calibration method

A developed simple static calibration system (SCS) was consisting of modified vials (4 ml) and the 100 μm PDMS SPME devices. The crystals of the PAH standards were inserted into the sinks at the bottom of each of the modified vial (see Fig. 1). System was capped and held until next day. The 100 μm PDMS fibers were conditioned before each analysis in the GC injector, under a helium stream (30 min at 250 °C). After that, the SPME device was inserted into the modified vials through a half-hole septum covered with a Teflon tape. The fibers were exposed for intervals ranging between 5 min and 70 h at 22 °C (air-conditioned) for the determination of the equilibrium time attainment (t_E) for each compound. The fibers were repeatedly exposed (five times) for the equilibrium time and then removed from the calibration vial, and thermally desorbed in the GC injector (for 6 min at 250 °C). The amount (n) of the analytes extracted into the fibers (at steady state) was determined by one-level calibration of the analytes in isooctane analyzed always before and after the fiber analysis. The optimized separation conditions were: initial oven temperature 30 °C for 6 min, ramped to 160 °C at the rate of 20 °C/min, ramped to 240 °C at the rate of 10 °C/min and at 240 °C held for 2 min, carrier gas flow was 0.8 ml/min.

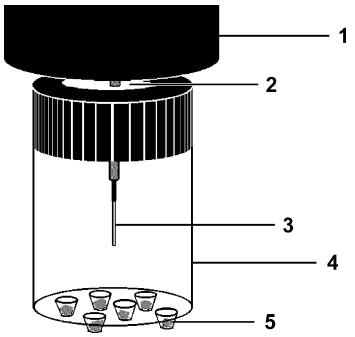

Fig. 1. Details of the calibration system used; (1) SPME holder; (2) septum; (3) SPME fiber with 100 μm PDMS polymer phases; (4) calibration vial; and (5) solid PAHs in sinks.

2.3. Determination of distribution coefficients for PAHs using LTPRI

The gaseous standards of *n*-alkanes were prepared by the standard stock solution volumetric injection (100 μl) of the *n*-alkanes in dichloromethane (20 μg ml^{-1}) into the sampling vials (40 ml, oven-heated at 200 °C and cooled before every injection). The solvent (dichloromethane) was let to evaporate under laboratory temperature (10 min), and then the vial was capped and held for 15 min at least. The 100 μm PDMS fibers were always conditioned in the GC injector, under a helium stream (30 min at 250 °C), and then inserted into the sampling vials through a half-hole septum covered with a Teflon tape. The fibers were exposed for 1, 5, 10, 30, 60, and 90 min at 22 °C (air-conditioned) for determining of t_E and then repeatedly exposed (five times) for ascertained time t_E (60 min) with a view to determinate of the K values. The fibers were always desorbed in the GC injector at 250 °C for 4 min. The K coefficients of *n*-alkanes were calculated as a rate of their peak areas from the analyses of the gaseous and the polymer phases recounted for the volume of the phases (6.9×10^{-10} m^3 for the 100 μm PDMS and 1×10^{-7} m^3 as an aliquot part of the gaseous-phase—directly injected by a gas-tight syringe). The calibration was realized by the same way as in case of the SCS method. The LTPRI indices of the *n*-alkanes and PAHs were calculated from repeatedly measured values of the retention times (t_r) of the *n*-alkanes and PAHs, and calculated by Eq. (2) as mentioned below. The K coefficients of the PAHs were calculated by Eq. (1) when the coefficients of a linear relationship (a and b) had been determined. The separation conditions were: Initial oven temperature 40 °C for 4 min, ramped to 260 °C at the rate of 18 °C/min, and at 260 °C held for 2 min, carrier gas flow was 1 ml/min.

Table 1
The conditions and the results; p is vapor pressure, C_g concentration of the analytes in the SCS, t_E is time of the equilibrium reaching and t_r is retention time

Compound	SCS—static calibration system method					LTPRI – method using chromatographic indices					Comparison		
	p at 25 °C (Pa) [3]	C_g at 22 °C (mg l^{-1})[a]	t_E (min)	log K	R.S.D. (%) ($n = 5$)	t_r (min)	LTPRI	log K	R.S.D. (%)[b] ($n = 5$)	R.S.D. (%) ($n = 5$)	T-stat[c]	T-crit (SCS)	T-crit (LTPRI)
Naphthalene	11	470	120	5.5	1.2	9.85	1199	5.2	0.28	4.4	1.35	2.02	2.57
Biphenyl	1.2	60.2	300	6.4	3.3	11.59	1399	6.0	0.02	8.3	0.83	2.02	2.57
Acenaphtylene	1.22×10^{-1}	6.16	540	7.2	2.4	12.20	1478	6.3	0.04	9.6	2.06	2.02	2.57
Acenaphtene	3.33×10^{-1}	16.5	540	6.8	5.3	12.46	1511	6.5	0.04	10.1	0.16	1.94	2.45
Fluorene	8.44×10^{-2}	4.43	1040	7.0	2.5	13.22	1616	6.9	0.03	11.6	−0.40	2.13	2.78
Phenanthrene	1.49×10^{-2}	8.44×10^{-1}	1410	7.8	3.3	14.63	1826	7.8	0.03	14.0	−0.50	2.13	2.78
Anthracene	3.56×10^{-4}	2.05×10^{-2}	2255	8.2	4.3	14.70	1839	7.8	0.02	14.2	0.12	2.02	2.57
Flouranthene	1.23×10^{-3}	8.02×10^{-2}	∼4530	∼8.4	∼	16.39	2061	8.7	0.01	16.2	∼	∼	∼
Pyrene	6.12×10^{-4}	3.92×10^{-2}	∼4530	∼8.2	∼	16.74	2092	8.9	0.01	16.5	∼	∼	∼

[a] The Clausius–Clapeyron equation was applied to converting of tabulate values of vapor pressure to vapor pressure at sampling temperature.
[b] R.S.D. of repeated injection by determination of LTPRI indices.
[c] The heteroscedastic t-test for the double-sided distribution and two samples with unequal variance.

2.4. Sampling of indoor and outdoor air

The 100 μm PDMS fibers were conditioned several times before the extraction and the resulting blank was analyzed on the GC/MS system in a selected ion recording (SIR) mode in order to ensure that no contaminants were presented. The fibers were exposed in laboratory air for 540 and 650 min at 22 °C, or in ambient air for 68 h at outdoor temperature (6.8–19.1 °C). The fibers used for the outdoor air sampling were always protected by aluminum foil during the sampling. For transfer of the exposed fibers a protective Teflon cover was applied. The exposed fibers then were analyzed on the GC/MS (SIR) system under the same conditions as in case of the SCS. The mass spectrometer detected the following masses: 128 (naphthalene), 152 + 154 (biphenyl, acenaphthene, acenaphthylene), 166 (fluorene), 178 (phenanthrene, anthracene), 202 (fluoranthene, pyrene).

3. Results and discussion

3.1. Determination of K by the static method

Thanks to layout in the SCS (equilibrium concentration of PAHs was equalized to vapor pressure at given conditions) the competitive adsorption processes on the walls were eliminated. At the constant temperature was not possible to change the concentration of PAHs in the system (see Table 1), therefore it was necessary a high sorption capacity and the linear relationship between K values and concentration of analytes in wide concentration range presup-

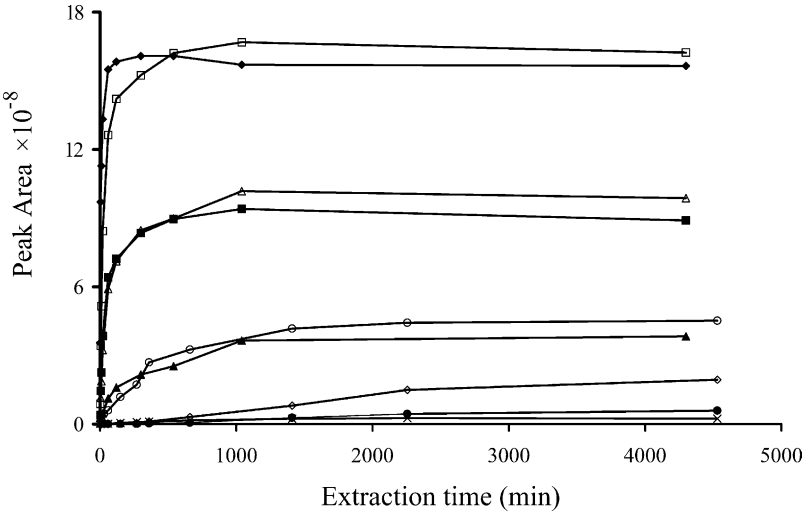

Fig. 2. Extraction time profile for extraction of PAHs from static calibration system by 100 μm PDMS SPME polymer phases. (◆, naphthalene; □, biphenyl; ■, acenaphtylene; △, acenaphtene; ▲, fluorene; ○, phenanthrene; ×, anthracene; ◇, flouranthene; ●, pyrene).

posed [17]. The extraction time profile showed that a very long time was necessary for attainment of the equilibrium in the SCS when the 100 μm polydimethylsiloxane phases had been used (see Fig. 2). The times of equilibrium attainment, the logarithm of distribution coefficients of tested PAHs and their relative standard deviation (R.S.D.%) are summarized in Table 1 along with their concentrations in the SCS and the vapor pressure values [3].

3.2. Determination of K by LTPRI method

There is the linear relationship (Eq. (1)) between measured log K (air/PDMS) values of the analytes and their LTPRI indices that is essential for determination of unknown values of the distribution coefficients [15].

$$\log K = a + b(\mathrm{LTPRI}) \quad (1)$$

where K are the distribution coefficients, a, b are the coefficients of linearity and LTPRI are the linear temperature–programmed retention indexes. The experimentally measured relationship is characterized by parameters $a = 0.2906$ and $b = 0.0041$ and $r^2 = 0.9917$. Substituting the LTPRI indices of any tested compounds established under same conditions into Eq. (1) we can estimate their log K values. The LTPRI indices were calculated by Eq. (2) [14].

$$\mathrm{LTPRI} = 100 \times \left(\frac{t_{r(A)} - t_{r(n)}}{t_{r(n+1)} - t_{r(n)}} \right) + 100n \quad (2)$$

where $t_{r(A)}$ is the analyte retention time, $t_{r(n)}$ is the retention time of the n-alkane eluting directly before $t_{r(A)}$, $t_{r(n+1)}$ is the retention time of the n-alkane eluting directly after $t_{r(A)}$, and n is the number of carbon atoms for $t_{r(n)}$. Table 1 shows retention times, LTPRI indices, and log K of the PAHs. Typical relative standard deviations of retention times for repeat injections yielded no more than 0.30%. A relatively good agreement between the log K values that were determined by both methods is summarized in the last three columns of Table 1.

3.3. Analysis of indoor and outdoor air samples

The experimentally determined distribution coefficients of PAHs and biphenyl were used for approximate quantification of these contaminants in both indoor and outdoor air samples. The responses of all analytes (recorded in a selected ion-monitoring mode) under described conditions were much higher than their detection limits. Therefore, the method could be applied for screening of PAHs in air samples at environmental concentration levels. When we used our experimental log K values for the quantification of the studied compounds in both of surroundings, concentration of the analytes had ranged between approximately 0.2 ng m^{-3} for pyrene and 100 ng m^{-3} for naphthalene.

4. Conclusion

The high concentrations of the analytes, impossibility to change them and a very slow achievement of the equilibrium belonged to main disadvantages of the used static calibration system. Although the 100 μm PDMS polymer phases offer the high sensitivity for the sampling of PAHs in ambient air, time necessary to establish the equilibrium (especially at higher concentration levels) is very long, and the static conditions cannot be kept always. Nevertheless, the method could be sufficient for screening of the PAHs in either indoor or ambient air, especially when the higher concentration level of the analytes are expected.

Acknowledgements

The authors thank Prof. Ladislav Omelka from Department of Physical & Applied Chemistry, Faculty of Chemistry, Brno University of Technology for discussion concerning theoretical basis of the used calibration system. Ministry of Agriculture of the Czech Republic supported this study (project M03-00-1).

References

[1] M. Chai, J. Pawliszyn, Environ. Sci. Technol. 29 (1995) 693.
[2] J. Namiesnik, B. Zygmunt, A. Jastrzebska, J. Chromatogr. A 885 (2000) 405.
[3] Compendium Method TO-13A, second ed., US EPA, Cincinnati, OH, 1999.
[4] J.O. Allen, A.F. Sarofim, K.A. Smith, Polycyclic Aromat. Compd. 13 (1999) 261.
[5] A.H. Ackerman, R.J. Hurtubise, Talanta 52 (2000) 853.
[6] M. Gehrke, S. Kapila, P. Nam, V. Flanigan, Chemosphere 43 (2001) 479.
[7] J. Koziel, M. Jia, A. Khaled, J. Noah, J. Pawliszyn, Anal. Chim. Acta 400 (1999) 153.
[8] J.A. Koziel, M. Odziemkowski, J. Pawliszyn, Anal. Chem. 73 (2001) 47.
[9] L. Lassagne, V. Jacob, P. Desuzinges, F. Tripoli, P. Kaluzny, P. Baussand, P. Foster, Fresenius Environ. Bull. 10 (2001) 381.
[10] D. Gorlo, L. Wolska, B. Zygmunt, J. Namiesnik, Talanta 44 (1997) 1543.
[11] P.A. Martos, J. Pawliszyn, Anal. Chem. 69 (1997) 206.
[12] J. Ai, Anal. Chem. 69 (1997) 1230.
[13] R.J. Bartelt, B.W. Zilkowski, Anal. Chem. 71 (1999) 92.
[14] V. Pacáková, L. Feltl, Chromatographic Retention Indices an Aid to Identification of Organic Compounds, Ellis Horwood Ltd., New York, 1992, p. 21.
[15] P.A. Martos, A. Saraullo, J. Pawliszyn, Anal. Chem. 69 (1997) 402.
[16] K. Kolář, M. Ciganek, Z. Šimek, in: I. Mašek (Ed.), Proceedings of the ICS-UNIDO Workshop on Technology and Processes for Sustainable Development and Pollution Reduction/Prevention, Poster Publishers, Brno, Czech Rep., 2002, p. 261.
[17] K. Gill, W.A. Brown, Anal. Chem. 74 (2002) 1031.