Indirect determination of low vapour pressures using solid-phase microextraction—application to tetrachlorobenzenes and tetrachlorobenzyltoluenes ☆

Albrecht Paschke*, Uwe Schröter, Gerrit Schüürmann

Department of Chemical Ecotoxicology, UFZ Centre for Environmental Research Leipzig, Permoserstrasse 15, 04318 Leipzig, Germany

Available online 22 January 2005

Abstract

There is still a gap of reliable vapour pressure data at ambient temperature for low volatile organic substances due to the difficult and time-consuming determination using the classical methods. Static headspace extraction with a solid-phase microextraction (SPME) fibre in combination with gas chromatographic analysis provides an inexpensive tool for the indirect determination of low vapour pressures down to 10^{-5} Pa. The procedure consists of two steps: (a) exposure of SPME fibre in the headspace above the test chemical over minutes to hours and (b) desorption and quantification of extracted amount. The calibration was performed using low volatile reference substances with well-known vapour pressures. A good correlation was found between substance uptakes of SPME fibre and vapour pressures. The method was applied, e.g. to tetrachlorobenzenes and to selected tetrachlorobenzyltoluenes with questionable vapour pressures. We obtained values between 0.98 and 13.5 Pa for the former and results between 0.13 and 0.68 mPa for the latter group of congeners. The scope of the method can be extended to substances with even lower vapour pressures, provided that reliable reference data are available.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Vapour pressure; Solid-phase microextraction; Chlorobenzenes; Hexachlorocyclohexane isomers; DDT; Polychlorinated biphenyls; Tetrchlorobenzyltoluenes

1. Introduction

The vapour pressure of a chemical is one of the key parameters for the prediction of its behaviour and fate in the environment [1–3]. But for many low volatile organic substances, which are considered as potential pollutants especially due to their persistence and bioaccumulation potential [4], reliable vapour pressure data at ambient temperature are often rare [3,5–7]. The tetrachlorobenzenes (TetraCBs) are such cases with large differences between reported values [3,7]. For 1,2,4,5-TetraCB, e.g., they range from 0.62 to 10.1 Pa. The main reason for incomplete/inaccurate data seems to be the difficult and time-consuming determination of low vapour pressures using the classical direct methods, namely the effusion techniques and the gas saturation method [8,9]. More rational indirect methods are based either on measuring evaporation rates or gas chromatographic (GC) retention times [9–11] and require the use of one or several reference compounds whose vapour pressures are accurately known over the whole temperature range investigated. A serious source of errors of these indirect methods regarding low volatile compounds is the extrapolation of results from high-temperature measurements to ambient conditions and the selection of appropriate reference compounds and/or relaible vapour pressure data for them. van Haelst et al. [12], for example, obtained with the GC method (using relative retention times) for each of the tetrachlorobenzyltoluenes (TCBTs) studied vapour pressures in the order of 5–14 mPa or of 0.1–0.3 mPa, depending on the use of either diphenylmethane or p,p'-DDT as reference substance.

The aim of our study was to demonstrate that solid-phase microextraction (SPME) from the vapour phase above the pure substance in combination with gas-chromatographic analysis can be used (without further sophisticated equipment) for the determination of low vapour pressures at environmentally relevant temperatures. Over the last 10 years, SPME has become a widely used pre-concentration tool, advantageously applicable for headspace analysis of various classes of organic compounds in different aqueous samples, biological fluids, solvent extracts and solid materials [13–15]. Physicochemical applications of SPME have also been reported, including the determination of partition coefficients of organic substances in the two-phase systems water/air [16–17] and octanol/air [18]. Moreover, polydimethylsiloxane-coated SPME fibres have already been used to estimate the vapour pressures of selected crop protection agents [19] or fragrance [20]. But in contrast to these applications we make directly use of the uptake rate of the SPME fibre.

Ai [21] derived and verified experimentally that the uptake rate of a chemical in the SPME fibre is proportional to its concentration in the headspace of a closed system (vial). Thereby he assumed (as a first approximation) a constant concentration in the headspace, i.e. a stationary state where the substance uptake into the fibre coating is immediately compensated by additional substance evaporation. We follow this consideration and assume in addition that the substances under investigation obey the ideal-gas equation. This is most likely due to their small headspace concentrations (in the range of mg to μg per m^3). Consequently, the fibre uptake rate of a substance is proportional to its vapour pressure. The presence of an excess of a foreign gas (air) in the headspace does not change this relationship (cf. the respective derivations in ref. [22]).

2. Experimental

2.1. Materials

The chemicals used in this study either as reference or target compounds were α-hexachlorocyclohexane (α-HCH), β-HCH, δ-HCH, 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (*p,p*′-DDD), 1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene (*p,p*′-DDE) as analytical-standard grade, pentachlorobenzene (PentaCB) and 1,2,3,4-tetrachlorobenzene (TetraCB) >99% pure from Riedel-de Haën (Seelze, Germany); lindane (γ-HCH) >99.5% pure, 1,2,4,5-TetraCB and 1,2,3,-trichlorobenzene (TriCB) >98% pure from Merck (Darmstadt, Germany); 1,2,3,5-TetraCB and 1,3,5-TriCB >99% pure from Fluka (Buchs, Switzerland); hexachlorobenzene (HCB) >99% pure and 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (*p,p*′-DDT) >98% pure from Aldrich (Dorset, UK); and finally the following polychlorinated biphenyls (PCB) and TCBT congeners >99.5% pure from Promochem (Wesel, Germany): 2,4,4′-

trichlorobiphenyl (PCB 28), 2,2′,5,5′-tetrachlorobiphenyl (PCB 52), 2,2′,4,5,5′-pentachlorobiphenyl (PCB 101), 2,2′,3,4,4′,5′-hexachlorobiphenyl (PCB 138), 2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB 153), 2,2′,3,4,4′,5,5′-heptachlorobiphenyl (PCB 180), 2,2′,4,4′-tetrachloro-3-benzyltoluene (TCBT 21), 2,2′,4,4′-tetrachloro-5-benzyltoluene (TCBT 22), 2,2′,4,5′-tetrachloro-5-benzyltoluene (TCBT 25), 2,2′,4,6′-tetrachloro-3-benzyltoluene (TCBT 27), 2,2′,5,5′-tetrachloro-4-benzyltoluene (TCBT 36), 2,3′,4,4′-tetrachloro-5-benzyltoluene (TCBT 52), 2′,3,4,4-tetrachloro-6-benzyltoluene (TCBT 74), 2′,3,4,6′-tetrachloro-6-benzyltoluene (TCBT 80).

Hexane, used as solvent for the preparation of liquid standards, was from Merck (Darmstadt, Germany) in the quality for organic trace analysis.

The two SPME fibres used in this study (see Section 2.2 for details) were purchased together with a manual SPME fibre holder from Supelco (Taufkirchen, Germany). The fibres were conditioned before use according to the instructions of the manufacturer and were checked for no carryover during the experiments.

2.2. Headspace solid-phase microextraction

Some milligrams of each pure test chemical (both target and reference compounds) were sealed in glass vials (10 mL). The vials were deposited typically overnight at room temperature (23–25 °C; air-conditioned) for establishing a nearly saturated headspace atmosphere due to sublimation of test substance. The SPME fibre was inserted through the vial septum and moved out of the needle housing into the headspace. After predetermined sampling times, ranging from minutes to hours, the fibre was retract, removed from the vial and immediately injected in the GC.

The shortest possible fibre exposure time to surpass the limit of quantification for each substance can be found by some initial tests or simply by leaving-out the uncertain results from the initial fibre uptake phase.

For selecting the more sensitive fibre type for further investigations we tested the uptake capacity of a fibre coated with 100 μm polydimethylsiloxane (PDMS) against a fibre coated with 65 μm Carbowax-divinylbenzene (CW-DVB). The results from the static exposure of both fibres (separately) in the saturated headspace above hexachlorobenzene for several period of time indicated clearly the fibre coated with CW-DVB as the one with the higher uptake capacity. After one hour exposure time it had already extracted the 1.3-fold, after 24 h the 2-fold and after 82 h the 3-fold amount taken up by the PDMS fibre.

2.3. Instrumental analysis

All analyses were performed with a gas chromatograph HP 5890 II equipped with a split/splitless injector, an auto-sampler 7673 and a MS detector 5971. Single ion monitoring

was used to record the chromatograms. The target analytes desorbed from the SPME fibre and those injected directly afterward as standard solutions in hexane (1 μL) for calibration of the GC response were separated on a 50 m × 0.32 mm i.d. CP-Sil 8CB-MS column coated with 0.12 μm film (Chrompack/Darmstadt, Germany). The injector was programmed to return in split mode 2 min after SPME fibre insertion and 1 min after liquid injection. As carrier gas helium 5.0 was used with a constant column flow of 1 mL/min. The injector temperature was held constant at 250 °C. The GC oven temperature program was: 60 °C for 2 min, ramped at 30 °/min to 150 °C, then at 4 °/min to 280 °C, hold for 20 min. The transfer-line temperature was 280 °C.

The GC response for the substance under consideration was calibrated by injecting aliquots of five to seven different standard solutions (in hexane) via auto-sampler.

2.4. Data evaluation

In a first step a linear regression of quantified fibre-extracted amounts versus exposure time was performed to obtain the fibre uptake rates from the slope (for both reference and target substances). Subsequently, a calibration line was established using the uptake rates of reference compounds vs. their tabulated vapour pressures.[1] Finally, the inverse of this calibration function was used to calculate the vapour pressure of target substances from the determined uptake rates.

3. Results and discussion

3.1. Uptake rates with the CW-DVB fibre

For substances with a vapour pressure larger then 1 Pa it has turned out to be sufficient to expose the CW-DVB fibre in the saturated headspace above the substance for seconds only to extract quantifiable amounts (∼1 ng under the actually chosen analytical conditions) and thus the SPME was restricted to periods of 2–10 min. A linear uptake can be assumed during this period of time. It is confirmed by the resulting correlation coefficients r between amount extracted, m_f, and t that are >0.99 for all substances. The slope of the regression line yields the uptake rate.

For compounds with a vapour pressure smaller then 0.1 Pa it was necessary to expose the CW-DVB fibre at least 10–15 min in the headspace to extract 0.1–1 ng. The longest extractions times in this study were typically 60–120 min. Also here we obtained linear fibre uptakes with r values >0.99.

---

[1] One has to pay attention to the selection of appropriate reference pressures at the temperature of investigation, i.e. the sublimation pressures for solid substances (P^{SV}) and the vapour pressures for liquids (P^{LV}). Moreover, one should not mistake the later value for the so-called "vapour pressure of the subcooled liquid" which is often found in literature and must be recalculated into the sublimation pressure before use in calibration.

Table 1
Vapour pressures, P^{SV}, of reference substances (at 25 °C), taken from literature and their uptake rates, dm_f/dt, in the CW-DVB fibre (with standard deviation)

Substance (abbreviation)	P^{SV} (mPa)	dm_f/dt (ng/min)
1,3,5-TriCB	20,500[a]	560.0 ± 10.9
1,2,3-TriCB	14,100[a]	348.2 ± 4.9
PentaCB	209[a]	49.93 ± 0.24
HCB	1.8[b]	0.0849 ± 0.0016
α-HCH	6.3[c]	0.5446 ± 0.0060
β-HCH	0.076[c]	0.0077 ± 0.0001
γ-HCH	2.8[c]	1.4410 ± 0.0138
δ-HCH	4.5[c]	0.3340 ± 0.0056
p,p'-DDT	0.045[c]	0.0075 ± 0.0002
p,p'-DDE	0.87[d]	0.0700 ± 0.0008
p,p'-DDD	0.13[d]	0.0141 ± 0.0002
PCB 28	16[e]	1.5166 ± 0.0367
PCB 52	4.97[e]	0.8956 ± 0.0201
PCB 101	1.6[f]	0.3330 ± 0.0137
PCB 138	0.158[e]	0.0478 ± 0.0003
PCB 153	0.12[g]	0.0449 ± 0.0002

[a] Ref. [24].
[b] Ref. [25].
[c] Ref. [26] (value at 25 °C linear interpolated from the data).
[d] Ref. [27].
[e] Ref. [28].
[f] Ref.[29].
[g] Ref. [30].

We have tested the reproducibility of SPME after 60 min for γ-HCH as substances with a relatively high vapour pressure and with β-HCH having one of the lowest P^{SV} values (within the actual set of reference compounds, cf. Table 1). From three extractions each we obtained a relative standard deviation of 2.2% with γ-HCH and 0.14% with β-HCH.

The obtained fibre uptake rates were summarized in Tables 1 and 2 for the reference and target substances, respectively.

3.2. Correlation between fibre uptake rates and vapour pressures

The use of the whole data set for the linear regression analysis between the fibre uptake rates of the reference

Table 2
Uptake rates of the CW-DVB fibre with target substances (at 23–25 °C; with standard deviation) and vapour pressures, P^{SV}, at 25 °C calculated from them using the calibration function

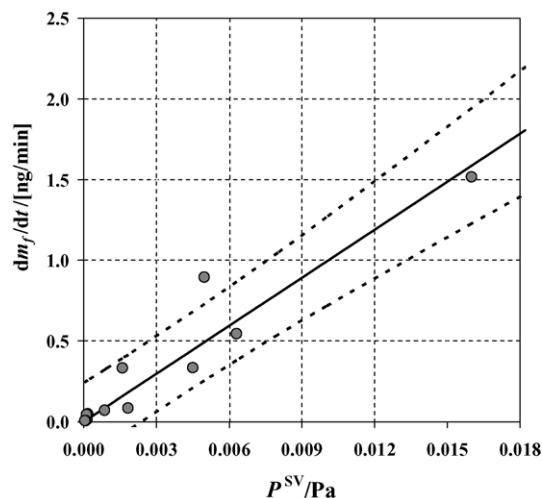| Substance (abbreviation)	dm_f/dt (ng/min)	P^{SV} (mPa)
1,2,4,5-TetraCB	25.98 ± 0.44	981
1,2,3,4-TetraCB	276.0 ± 2.7	10,420
1,2,3,5-TetraCB	357.2 ± 8.4	13,500
TCBT 21	0.0317 ± 0.0005	0.320
TCBT 22	0.0676 ± 0.0021	0.682
TCBT 25	0.0541 ± 0.0004	0.546
TCBT 27	0.0462 ± 0.0011	0.466
TCBT 36	0.0286 ± 0.0003	0.288
TCBT 52	0.0156 ± 0.0002	0.158
TCBT 74	0.0126 ± 0.0002	0.127
TCBT 80	0.0233 ± 0.0006	0.235

Fig. 1. Plot of fibre uptake rates vs. sublimations pressures for the subset of reference compounds with $P^{SV} \leq 0.016$ Pa (including regression line and 95% confidence interval).

Fig. 2. Comparison of actually measured P^{SV} of selected TCBT congeners with published data (filled circles symbolise this work; triangles show data from ref. [12] obtained with the relative retention time method using p,p'-DDT as reference and squares represent data from ref. [12] determined using the retention index method). For this presentation we have converted the liquid vapour pressure data from ref. [12] into sublimation pressures using the melting point of the individual TCBT congener (provided by Promochem, the TCBT supplier) and, in lacking of experimental values, a general estimate of $55\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for the entropy of fusion (which was determined for PCB congeners [9]).

substances and their tabulated P^{SV} values would cause a not very meaningful cluster correlation due to the inhomogeneous distribution of data points along the pressure axis. Therefore we divided the data set into two subsets above and below 0.016 Pa and included PCB 28 in both subsets as lower and upper limit, respectively. In addition we had to eliminate lindane as an outlier from the data.

In the upper pressure range our calibration is statistically not well-founded due to the limited number of data points ($n = 4$). Nevertheless we obtained a significant relationship: $\mathrm{d}m_f/\mathrm{d}t/(\mathrm{ng/min}) = 26.49\,(\pm 1.25) \cdot P^{SV}/\mathrm{Pa}$ with a correlation coefficient of 0.9930. With the inverse form we have estimated the vapour pressures of the TetraCBs from their fibre uptake rates. The values for 1,2,4,5-TetraCB and 1,2,3,5-TetraCB, listed in Table 2, are in the order of magnitude of the few values reported at ambient temperature [3,7]. For 1,2,3,4-TetraCB we obtained the 2-fold value of the previously published P^{SV} datum [3,7].

For the lower pressure range ($n = 12$) we obtained the following linear relationship: $\mathrm{d}m_f/\mathrm{d}t\ (\mathrm{ng/min}) = 99.09\ (\pm 7.72) \cdot P^{SV}/\mathrm{Pa}$ with a correlation coefficient of 0.9507. (In the course of the data analysis, the intercept of the linear relationship has turned out to be insignificant and was set to zero for the final regression.) Fig. 1 shows the calibration line and the related 95% confidence limits. The calculated sublimation pressures of the TCBTs are listed in Table 2. As can be seen in Fig. 2, our results are comparable with the values obtained by van Haelst et al. [12] using p,p'-DDT as reference compound for the relative GC retention time method and alternatively with the retention index method. Only the application of a direct vapour-pressure measuring procedure, e.g. the gas saturation method [8], could provide more insight here.
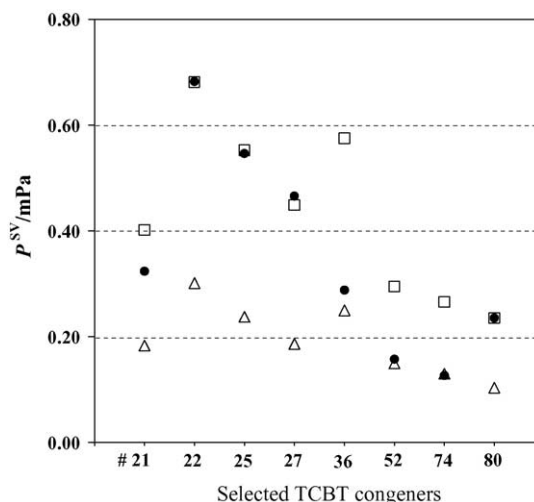
A preliminary test with PCB 180 shows that the scope of the actual method can be extended to substances with even lower vapour pressures. The uptake rate of PCB 180 in the CW-DVB fibre is ~ 0.0038 ng/min. This yields a vapour pressure of approximately 3.8×10^{-5} Pa. By extension of the extraction time, that is no problem due to the simplicity of the actual procedure, it will be possible to determine vapour pressures $< 10^{-5}$ Pa. But for long extraction times one should ensure a constant room temperature (or thermostatting) and take the drift of the detector signal into account. Additional problems can arise when, for increasing the sampling capacity, several fibre-specimen of the same type should be used in parallel. Because of possible differences in the individual fibre efficiencies, observed with CW-DVB fibre type [23], it is necessary to cross-check the fibres with reference substances which render the intended range of vapour pressure measurements.

For substances with a well-known vapour pressure it seems to be possible to modify the described headspace-SPME method to determine the diffusion coefficient in air or the evaporation rate. A study considering these aspects is under way.

References

[1] C.F. Grain, in: W.J. Lyman, W.F. Reehl, D.H. Rosenblatt (Eds.), Handbook of Chemical Property Estimantion Methods: Environmental Behavior of Organic Compounds, American Chemical Society, Washington, DC, 1990 (chapter 14).

[2] R.R. Schwarzenbach, P.M. Gschwend, D.M. Imboden, Environmental Organic Chemistry, Wiley, New York, 1993.

[3] D. Mackay, W.Y. Shiu, K.C. Ma, Illustrated Handbook of Physical–Chemical Properties and Environmental Fate for Organic Chemicals, vols. I–V, Lewis Publishers, Boca Raton, FL, 1992–1997.

[4] J.B. Unsworth, R.D. Wauchope, A.W. Klein, E. Dorn, B. Zeeh, S.M. Yeh, M. Akerblom, K.D. Racke, B. Rubin, Pure Appl. Chem. 71 (1999) 1359, cf. also: http://www.chem.unep.ch/pops/.

[5] J. Altschuh, R. Brüggemann, in: D. Calamari (Ed.), Chemical Exposure Predictions, Lewis Publisher, Boca Raton, FL, 1993 (chapter 1).

[6] H.A. Bamford, J.E. Baker, D.L. Poster, Review of Methods and Measurements of Selected Hydrophobic Organic Contaminant Aqueous Solubilities, Vapor Pressures, and Air–Water Partition Coefficients, US Department of Commerce/National Institute of Standards and Technology, Gaithersburg, MD, 1998 (NIST Special Publication 928).

[7] W.Y. Shiu, K.C. Ma, J. Phys. Chem. Ref. Data 29 (2000) 41 and 387.

[8] Organisation for Economic Co-operation and Development: OECD Guideline for Testing of Chemicals No. 104: Vapour Pressure, Paris, 1995.

[9] A. Delle Site, J. Phys. Chem. Ref. Data 26 (1997) 157.

[10] B. Koutek, J. Cvačka, L. Streinz, P. Vrkičivá, J. Doubský, H. Šimonová, L. Feltl, V. Svoboda, J. Chromatogr. A 923 (2001) 137.

[11] T.M. Letcher, P.K. Naicker, J. Chromatogr. A 1037 (2004) 107.

[12] A.G. van Haelst, F.W.M. van der Wielen, H.A.J. Govers, J. Chromatogr. A 727 (1996) 265.

[13] Z. Zhang, J. Pawliszyn, Anal. Chem 65 (1993) 1843.

[14] J. Pawliszyn, Solid Phase Microextraction—Theory and Practice, Wiley-VCH, New York, 1997.

[15] J. Pawliszyn (Ed.), Applications of Solid Phase Microextraction, Royal Society of Chemistry, Cambridge, UK, 1999.

[16] J. Dewulf, H. van Langenhoven, P. Everaert, J. Chromatogr. A 830 (1999) 353.

[17] B.G. Bierwagen, A.A. Keller, Environ. Tox. Chem. 20 (2001) 1625.

[18] K. Treves, L. Shragina, Y. Rudich, Atmos. Environ. 35 (2001) 5843.

[19] T. Kröhl, R. Kästel, W. König, H. Ziegler, H. Köhle, A. Prag. Pestic. Sci. 53 (1998) 300.

[20] C. Acevedo, E. Sanchez, M.E. Young, R. Simpson, J. Food Eng. 59 (2003) 431.

[21] J. Ai, Anal. Chem. 69 (1997) 3260.

[22] K. Denbigh, Prinzipien des chemischen Gleichgewichts, 2. Aufl., Steinkopff, Darmstadt, 1974, pp. 163–165.

[23] A. Paschke, P. Popp, B. Vrana, in: W. Breh, J. Gottlieb, H. Höltzl, F. Kern, T. Liesch, R. Niessner (Eds.), Field Screening Europe 2001, Kluwer, Dordrecht, 2002, pp. 259–264.

[24] V. Roháč, V. Růžička, K. Růžička, M. Polednniček, K. Aim, J. Jose, M. Zábranský, Fluid Phase Equilibr. 157 (1999) 121.

[25] F. Wania, W.Y. Shiu, D. Mackay, J. Chem. Eng. Data 39 (1994) 572.

[26] E.W. Balson, Trans. Faraday Soc. 43 (1947) 54.

[27] K. Yoshida, T. Shigeoka, F. Yamauchi, Ecotoxicol. Environ. Safety 7 (1983) 179.

[28] L.P. Burkhard, A.W. Andren, D.E. Armstrong, Envrion. Sci. Technol. 19 (1985) 500.

[29] J.W. Westcott, T.F. Bidleman, J. Chromoatogr. 210 (1981) 331.

[30] W.Y. Shiu, D. Mackay, J. Phys. Chem. Ref. Data 15 (1986) 911.