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Using different types of capillary chromatographic columns as denudation traps: a comparison of sorption properties

M. Dudek, A. Kloskowski, L. Wolska, M. Pilarczyk, J. Namieśnik*

Department of Analytical Chemistry, Chemical Faculty, Technical University of Gdansk (TUG), 11/12 G. Narutowicza St., 80-952 Gdansk, Poland

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Abstract

The research presented concerns segments of capillary chromatographic columns of different types (WCOT, SCOT, PLOT) used as traps for collection of samples of volatile organic analytes from a stream of air utilizing the equilibrium denudation technique. During the model experiments (utilizing standard mixtures), values of the partition coefficients (K_{fs}) were determined for volatile organic compounds frequently occurring as pollutants of atmospheric air (benzene, toluene, ethylbenzene, *o*-xylene, chlorobenzene). The conducted research demonstrated that the stationary phase film thickness did not affect the partition coefficient value. It was also proved that there is no dependence between the manner of applying the stationary phase in the column and the partition coefficient value.

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1. Introduction

Atmospheric air is the human being's most basic environment, and therefore analyzing its composition is of fundamental significance for health protection. The basic problems connected with the analytics of atmospheric pollution are the result of low concentration levels of some of the compounds in the air and the heterogeneous character of the system. In order to meet the requirements, a number of passive [1–4] and dynamic [5,6] techniques of analyte isolation and/or enrichment have been invented. These techniques, although they make possible the

analysis of trace amounts of pollutants, also have some drawbacks. They don't allow one to determine the distribution of the pollutants between particular phases (dusts, aerosols) of the system. A search for an atmospheric analysis technique that would be at once compact and complex has led to the development of denudation techniques. The essence of the denudation phenomenon is the combination of two processes: the diffusion of gaseous air components to the surface of the retaining (enriching) medium, and their movement in the forced flow of the stream of gas [7,8].

The denudation methods of sample collection, like the dynamic methods, are characterized by a short time of sample acquisition as compared with the relatively long exposition time needed in the case of

*Corresponding author. Fax: +48-58-347-2694.

E-mail address: chemanal@sunrise.pg.gda.pl (J. Namieśnik).

passive methods [9]. Another advantage of denuders is the high level of selectivity of the enrichment process. The most basic advantage of the denudation methods over other methods is the aforementioned possibility of making a speciation analysis of the components present in the atmosphere [10–12]. Despite all these pros, denudation techniques are not as yet widely used in atmospheric pollution analytics. It seems that the main cause of this state of affairs are the difficulties connected with preparing these types of devices for work. In a classic denuder, the inner surface of the tube wall is covered with a sorption medium. The effectiveness and reproducibility of the enrichment process in such a device depends on the homogeneity of the sorption layer. After adsorbing the analytes, the retained compounds were released usually by washing out the retaining medium from the device. The subsequent use of the denuder required the replenishment or the reconstruction of the sorption layer, which was difficult to achieve in a reproducible manner. Therefore, the newer technical solutions began to utilize liquid sorption media [13–15] or thermostable organic polymers [16,17]. This latter option allowed for the use of thermal desorption at the analyte release stage without changing the sorption properties of the device, making it possible to utilize the trap again without going through the calibration stage. An additional advantage to this method of releasing the analytes from the trap is the elimination of organic solvents from the analytical procedure. However, covering the denuder wall with a homogeneous stationary phase film of suitable thickness poses difficulties [18,19].

The ideal, ready-made solution to this problem seems to be to utilize, as the sorption trap, a piece of a suitable, commercial capillary chromatographic column. In recent years several publications appeared describing this way of employing capillary columns, both in studying air [20–23] as well as water [24,25]. Some of the papers described their effectiveness in the process of focusing analytes before introducing the sample onto the head of the chromatographic column.

The main aim of this study was to compare the characteristics of denudation traps prepared of segments of different types of capillary chromatographic columns. The research was done employing the

method of equilibrium sorption [26], and determining the values of the partition coefficient of the analytes between the gaseous and the stationary phase (in the denuder).

2. Experimental

2.1. Chemicals and materials

The reagents utilized in the experiments (benzene, toluene, ethylbenzene, *o*-xylene, chlorobenzene) are classified as chromatographic standards and were purchased from Polish Chemical Reagents (Gliwice, Poland).

Segments (12 cm) of different types of capillary columns available on the market were employed as the denudation traps. More specific information is presented in Table 1.

The sorption trap used for calibrating the system was produced using a glass tube 105×4 mm (length×I.D.) filled with beds of solid sorbents: Tenax TA (100 mg, 35–60 mesh) purchased from Alltech (Lancashire, UK) and Carbotrap (50 mg, 20–40 mesh) purchased from Supelco (Bellefonte, USA). The sorbent beds were immobilized from both ends of the tube and separated from each other with plugs of silanized glass wool.

2.2. Gaseous standard mixture and chromatographic conditions

The model experiments were performed with appropriate gaseous standard mixtures, which were prepared using two techniques—the static and the dynamic. In the static method, liquid components of the standard mixture were introduced through a membrane into an appropriately prepared steel cylinder [27] where there was absolute pressure of 1 Pa. Next, the cylinder was filled with synthetic air (a mixture of nitrogen and oxygen) until the pressure reached 4 MPa. In order to ensure homogeneity of the mixture the bottle was positioned at a 45° angle and heated from below for 4 days.

In the case of the dynamic technique, the phenomenon of permeation into a stream of gas was utilized [28,29]. The respective system consisted of the following elements: compressed air

Table 1
Technical data concerning the capillary chromatographic columns from which the denudation traps were made

| Type of capillary column | Type of stationary phase | State of matter of stationary phase | Thickness of stationary phase film [μm] | Internal diameter of the capillary [mm] | Manufacturer |
|--------------------------|--------------------------|-------------------------------------|--|---|--------------------|
| WCOT 18 ^a | PDMS* | Liquid | 18 | 0.53 | Quadrex |
| WCOT 12 | PDMS | Liquid | 12 | 0.32 | Quadrex |
| SCOT 5 ^b | PDMS on a support | Liquid | 5 | 0.53 | Hewlett Packard |
| PLOT 10 ^c | Porapak Q** | Solid | 10 | 0.32 | Chromopack |

* Polydimethylsiloxane; ** styrene–divinylbenzene copolymer.

^a Wall coated open tubular.

^b Support coated open tubular.

^c Porous layer open tubular.

tank→purifier→dryer→generator. The purifier and the dryer were filled with beds of active carbon and a molecular sieves, 5 Å. The generator, together with the permeation containers placed in it, was kept at a temperature of 28.0 ± 0.1 °C during the generation of the gaseous standard mixture. The gas flow-rate was controlled with $0.05 \text{ cm}^3/\text{min}$ accuracy using a soap bubble flow meter.

The permeation rate, and therefore the concentration of the gaseous standard mixture components was determined using the gravimetric method (by finding the amount of mass lost by the permeation containers in ca. 30 days), and controlled independently using the chromatographic technique (by determining the amount of analytes captured in the sorption tube connected for a specific amount of time to the gaseous standard mixture generator). More precise data concerning the conditions in which the research and the chromatographic analysis were carried out are presented in Table 2.

2.3. Procedure

A study of the sorption characteristics of the denudation traps was performed in the TD–GC–FID system, the schematic diagram of which is shown in Fig. 1. The essential element of the measuring system is a thermal desorber of our own design [30]. The sealing of the sorption trap in the desorber was achieved by tightening it with cone shaped Teflon gaskets.

The heating chamber of the thermal desorber was placed inside the loop of the gas-tight, six-way valve.

The two valve positions made it possible to direct the stream of the gaseous standard mixture through the desorber chamber (continuous line for this valve position) or out of the system (the broken line). In the first case, sorption of analytes from the gaseous standard mixture stream occurred in the denuder. In the second valve position, the analytes trapped were released thermally and carried in the countercurrent through the carrier gas stream onto the head of the chromatographic column. Before each experimental cycle the denuder was conditioned at 200 °C in a stream of hydrogen.

The calibration of the system consisted of determining the dependence of the respective peak areas on the mass of analytes introduced into the system. In order to achieve this, the denuder in the above described system was replaced with a glass tube filled with a sorption bed. The glass tube was placed in the thermal desorber in such a way that the gaseous standard mixture stream entered from the end filled with the layer of the solid sorbent Tenax TA. Before each use the tube was conditioned at 250 °C in a stream of hydrogen.

3. Results and discussion

3.1. Enrichment of the analytes in the trap utilizing the equilibrium technique

In the equilibrium technique, a stream of the gas under study is passed through the denuder at a stable flow-rate and at given, stable temperature. The time

Table 2
The conditions for the experiments and the chromatographic analyses

| Denuder type | WCOT 18, SCOT 5 | WCOT 12, PLOT 10, SCOT 5 |
|---|--|--|
| Conditions for the experiments conducted | | |
| <i>gaseous standard mixture</i> | | |
| ➤method of production | static | dynamic |
| ➤standard mixture composition and the concentrations of the components [mg/m ³] | chlorobenzene; 747 benzene; 201 toluene; 380 ethylbenzene; 277 o-xylene; 224 | chlorobenzene; 295 |
| ➤gaseous standard mixture flow-rate | 1.00±0.05 cm ³ min ⁻¹ | 1.00±0.05 cm ³ /min |
| sorption time | From 1 min to 60 min | from 15 s to 60 min |
| sorption temperature | 28±1 °C | 28±1 °C |
| Conditions for the chromatographic analyses | | |
| gas chromatograph | GC 6000 Vega Series 2, Carlo Erba Instruments | |
| dosing system | thermal desorption | |
| desorption temperature | 200 °C | |
| desorption time | 3 min | |
| carrier gas | hydrogen (70 kPa) | hydrogen (35 kPa) |
| temperature program | 45 °C for 2 min 5 °C/min up to 100 °C 10 °C/min up to 250 °C 250 °C for 10 min 3 °C/min up to 270 °C 270 °C for 4 min | 35 °C for 1 min 7 °C/min up to 120 °C 10 °C/min up to 200 °C 200 °C for 4 min |
| column (length) | RSL-200 (60 m) | Rtx-1301 (30 m) |
| diameter | 0.32 mm | 0.32 mm |
| stationary phase thickness | 0.5 μm | 0.25 μm |
| detector | flame-ionization (FID) | |
| temperature | 250 °C | |
| Integrator | Chromatography Station for Windows—SCW 1.7 | CE Instruments DP 700 |

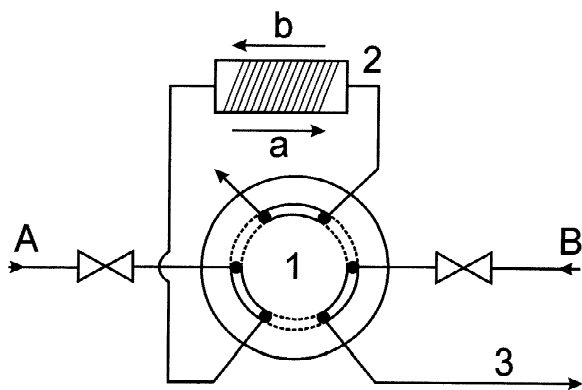


Fig. 1. Schematic diagram of the TD-GC system. 1—thermal desorber, 2—gas-tight six-way valve, 3—GC, A—gaseous standard mixture, B—carrier gas, a—sorption, b—desorption.

passing the stream of the studied gaseous medium through the denuder is chosen so that breakthrough of the trap would occur. The process of reaching the state of equilibrium by the system was followed by determining the amounts of the captured analyte in the function of the time for which the gaseous standard mixture was passed through the trap (so called sorption profiles).

During the initial stage, we find that the amount of analyte collected increases as the time of contact of the gaseous standard mixture with the retaining medium lengthens. The second stage is the straight line parallel to the time-axis, which represents the state of thermodynamic equilibrium between the gaseous standard mixture and the sorbent. This stage can be described with the following equation:

$$y = b \times t + a \quad (1)$$

where: y —amount of compound collected in the denuder [a.u.]; t —sorption time [min]; a —intercept [a.u.]; b —slope [a.u./min]

After reaching the equilibrium state, ‘ b ’ is close to zero and the straight line equation is simplified to the form $y = a$. Equilibrium amount of an analyte adsorbed under experimental conditions was equal to ‘ a ’ expressed in mass units, which was subsequently converted into equilibrium concentration of the analyte in the stationary phase, taking into account the volume of its film. The values of the partition coefficients K_{fs} ($K_{fs} = C_f/C_s$, where C_f and C_s are equilibrium concentrations of an analyte in the stationary phase and in the gas, respectively), were calculated for benzene, toluene, ethylbenzene, chlorobenzene and *o*-xylene.

There are two important, practical aspects of the experimental approach used in the paper:

- The method utilized is a direct one. Final values of the partition coefficients are obtained exclusively on the basis of GC determined concentrations of analytes in the gas stream after desorption from the stationary phase in the denuder (providing the volume of the stationary phase and the concentration of the initial standard mixture are known).
- Full concentration vs. sorption time profiles permit to determine another parameter essential in practical applications of the procedure, i.e. the minimum time needed for reaching the state of equilibrium between the two phases.

An alternative method of determination of partition coefficients by elution chromatography may be of some interest, particularly when performed using the same column, a piece of which serves as a denuder. We have already carried out some experiments and found that, despite its apparent advantages, the method is unsuitable in the case. The results of these investigations will be published elsewhere.

3.2. Comparison of the sorption properties of denuders with PDMS phase film of different thickness

For the purpose of this research, denuders with PDMS phase film of three different thicknesses (5, 12, 18 μm) were employed. A stream of the gaseous standard mixture was passed through the respective traps under the conditions given in Table 2. On the basis of the sorption profiles, experimental points, corresponding to the equilibrium state, were preliminarily selected. The final choice was made by statistical testing the significance of the difference of the slope, ‘ b ’, from zero (results of these tests are included in Table 3, on the basis of data obtained for chlorobenzene).

The determined values of the partition coefficients K_{fs} for all analytes under investigation have been collected in Table 4.

On the basis of the data collected in Table 4, one can say that the values of the partition coefficient for all analytes determined in denuders characterized by different PDMS phase film thickness are rather close.

Table 3

Linear regression analysis of the experimental points describing the equilibrium state, statistical assessment of the results obtained

| Compound | d [μm] | V [cm^3/min] | a [ng] | b [ng/min] | SD_a [ng] | SD_b [ng/min] | n | t_{crit} $f = n - 2$ | t_{calc} |
|---------------|--------------------------|-------------------------------------|-------------|-----------------|-----------------------|---------------------------|-----|----------------------------------|-------------------|
| Chlorobenzene | SCOT 5 | 0.5 | 1991 | 0 | 20 | 0.69 | 7 | 2.571 | 0.005 |
| | | 1 | 1030 | 0 | 49 | 1.1 | 9 | 2.365 | 0.008 |
| | WCOT 18 | 0.5 | 7370 | 0 | 120 | 1.2 | 9 | 2.365 | 0.200 |
| | | 1 | 3570 | 4 | 102 | 4.3 | 7 | 2.571 | 1.036 |
| | | 7 | 558 | -0.10 | 10 | 0.29 | 8 | 2.447 | 0.344 |

Where: d —thickness of the stationary phase covering the denuder walls; V —the flow-rate of the gaseous standard mixture stream; a —intercept; b —slope; SD_a —standard deviation ‘ a ’; SD_b —standard deviation ‘ b ’; n —the number of measuring points making up the equilibrium straight line (five parallel repetitions for each point).

Table 4

The values of the partition coefficients of analytes, determined using denuders with different thickness of the stationary phase film and selected literature data

| Column type, d [μm] | | \overline{K}_{fs} | | | | |
|---------------------------------------|----|---------------------|---------|---------|--------------|------------------|
| | | Chlorobenzene | Benzene | Toluene | Ethylbenzene | <i>o</i> -Xylene |
| SCOT | 5 | 3470 | 450 | 1080 | 2750 | 3570 |
| WCOT | 12 | 3450 | 440 | 1100 | 2770 | 3500 |
| | 18 | 3380 | 440 | 1120 | 2690 | 3500 |
| OTT (80)* | | n.a. | 410 | 1122 | n.a. | n.a. |
| SPME (100)* | | n.a. | 345 | 967 | 3468 | 3388 |
| Trap packed with PDMS* | | n.a. | 419 | 1106 | n.a. | n.a. |

where \overline{K}_{fs} —mean partition coefficient. * Literature data (n.a.—not available).

The significance of the differences between the values of the determined partition coefficients was tested by means of the *t*-Student's test, having earlier compared the significance of the variation differences between the data sets using the *F*-Snedecor test (not shown).

The calculated experimental values F_{calc} were, in each case, smaller than the critical value F_{crit} found in the tables for the numbers of degrees of freedom ($n_1 - 1$ and $n_2 - 1$) and probability level 95%. Similarly, the calculated experimental values t_{calc} were, also in each case, smaller than the critical value t_{crit} found in the tables for a number of degrees of freedom ($f = n_1 + n_2 - 2$) and probability level 95%. The differences between the values of the partition coefficients K_{fs} for all analytes, determined for denudation traps with stationary phase film of differing thickness, are not statistically significant. One can therefore accept the hypothesis that the thickness of the stationary phase film in the denuder does not influence the value of the partition coefficient, when determined by the method employed in this study.

It should be noted that the values of the partition coefficients obtained as a result of the application of the SCOT type denuder do not differ from the corresponding values of the coefficients determined for the WCOT type denuder. This leads to the conclusion that the method of applying the stationary phase onto the column walls (direct or on a support) does not influence the value of the partition coefficient.

3.3. Comparison of the obtained values of partition coefficients (K_{fs}) with data found in literature

Averaged values of the partition coefficients determined for the denuders with PDMS phase film of differing thickness were compared with the available literature data. In Table 4 the obtained results (K_{fs}) were put side by side with results obtained utilizing: a denudation trap with film 100 μm thick (OTT) [19], SPME fiber covered with film 100 μm thick [31], and a trap packed with 100% PDMS [32].

A comparison of the partition coefficient values for benzene and toluene determined utilizing denuders of the WCOT and SCOT types and a denuder with 80 μm film of cross-linked PDMS confirms the hypothesis about the lack of influence of the thickness of the sorption phase film in the trap on the partition coefficient value. The partition coefficient K_{fs} is, therefore, under the conditions of stable temperature, a value characteristic for the given analyte and the type of stationary phase.

The partition coefficient values of selected analytes obtained as a result of research carried out utilizing different isolation techniques (denudation, passive, and dynamic) with traps containing a sorption bed in the form of PDMS phase film are similar. Fig. 2 presents the relationship between the partition coefficient values determined using a denudation trap and a SPME fiber.

The dependence is linear with the slope close to one and yields high values of the determination

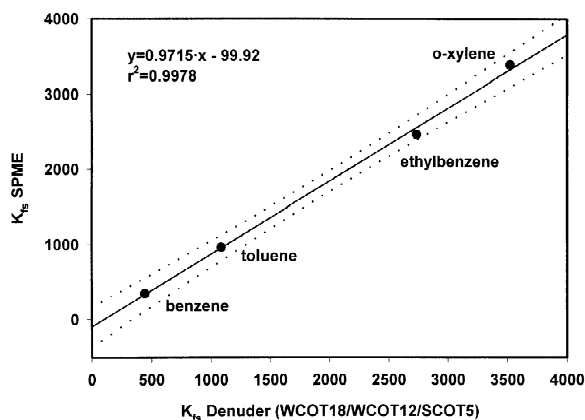


Fig. 2. The relationship between the values of the partition coefficient K_{fs} determined using a denudation trap and a SPME fiber. (PDMS was used in both cases as the sorption medium).

coefficient, $r^2 = 0.9978$. The calculated value (for formal reasons) of the intercept ($a = -99.92$) does not differ from zero in any statistically significant way, as is confirmed by the confidence interval (95%), shown on the diagram with a dotted line. The obtained results (K_{fs}) were analogically compared with the values determined using a trap packed with a 100% PDMS bed. In this case, the value of the slope, $b = 0.9519$, and the value of the determination coefficient $r^2 = 0.9975$.

The value of the determination coefficient close to one proves a very high correlation between the coefficients determined as a result of utilizing different enrichment techniques. The stable value of the coefficient of the partition of the analytes between the gaseous phase and PDMS film is significant from the point of view of analytics, since it makes it possible to use in calculations the results (K_{fs}) obtained by other authors, also in the case of their

using different isolation techniques. As a result, the analytical procedure can be limited to the calibration and sampling stages, and therefore significantly shortened.

3.4. Comparison of the sorption properties of a denuder covered with the liquid phase of an organic polymer (PDMS) and a denuder with a solid sorption layer (PORAPAK Q)

The sorption properties of denuders covered with the liquid phase of an organic polymer (PDMS) and those with a solid sorption layer (PORAPAK Q) were compared by determining the partition coefficients for chlorobenzene. The study was conducted using a standard mixture generated dynamically (Table 2). Determining the amount of the analyte adsorbed in the trap at the equilibrium state was done in the manner described earlier (3.2). Table 5 presents the results of the regression analysis of the experimental points describing the equilibrium state in denudation traps (PLOT 10, WCOT 12) together with their statistical assessment.

Since $t_{calc} < t_{crit}$, it can be assumed that the slope is not different from zero in any statistically significant way. The calculated values of the partition coefficients K_{fs} for chlorobenzene are presented in Table 6.

It is easily seen that the value of the partition coefficient for chlorobenzene is several times greater in the case of the denudation trap with the sorption phase made out of a porous polymer (PORAPAK Q) than in the case of applying a liquid polymer (PDMS) as the stationary phase. This shows that a PLOT denuder is characterized by higher efficiency of enrichment per a unit volume of the stationary phase than a WCOT or a SCOT denuder. However,

Table 5

The statistical evaluation of the results obtained from the study of the chlorobenzene sorption process in a type PLOT (10 μm) i WCOT (12 μm) denuder after the state of thermodynamic equilibrium was reached

| Type of denuder | d [μm] | a [ng] | b [ng/min] | SD_a [ng] | SD_b [ng/min] | n | t_{crit} $f = n - 2$ | t_{calc} |
|-----------------|--------------------------|-------------|-----------------|----------------|--------------------|-----|---------------------------|------------|
| PLOT | 10 | 7464 | 0.1 | 232 | 0.35 | 5 | 3.182 | 0.393 |
| WCOT | 12 | 3460 | 11 | 130 | 8.4 | 4 | 4.303 | 1.265 |

Table 6

The partition coefficient values obtained for chlorobenzene and the time necessary for the equilibrium state to be reached while using denuders with liquid (PDMS) and solid (PORAPAK Q) stationary phase

| Stationary phase | State of matter of the stationary phase | d [μm] | t [min] | \overline{K}_{fs} |
|------------------|---|-----------------------|-----------|---------------------|
| PDMS | Liquid organic polymer | 5, 12, 18 | 5–10 | 3400 |
| PORAPAK Q | Solid porous polymer | 10 | > 100 | 21 660 |

t —time necessary to achieve equilibrium.

the time necessary to achieve equilibrium presents a severe drawback, since the state of equilibrium is an important parameter from the point of view of applying such denuders in analytical practice. The time after which the system reaches the equilibrium state in the case of a PLOT type denudation trap is 10 to 20 times longer than in the case of PDMS denuders with thinner (5 μm) and thicker (12–18 μm) stationary phase film, respectively. Nonetheless, a denuder with a PLOT type stationary phase can be utilized for isolation and enrichment of analytes from air in long term research projects, for example.

4. Conclusions

This paper presents the results of a study of the sorption properties of denudation traps prepared out of segments of different types of commercial capillary chromatographic columns. In the equilibrium sorption technique applied, the knowledge of the values of the analyte partition coefficients (K_{fs}) makes it possible to determine their concentration in the sample being analyzed on the basis of the amount of analyte collected in the trap. The values of coefficients of partition between the gaseous phase and the stationary phase film were determined for group BTEX analytes, as well as chlorobenzene, by utilizing denudation traps of the following types: WCOT (PDMS, 12 and 18 μm) SCOT (PDMS, 5 μm) and PLOT (PORAPAK Q, 10 μm). The comparison of the obtained results with those by other authors leads to the conclusion that the values of the partition coefficients of analytes do not depend on the thickness or the manner of applying the stationary phase film. Also, no dependence was

found, in the case of the PDMS stationary phase, between the partition coefficient value and the analyte isolation technique.

The study of the sorption properties of denudation traps utilizing a segment of a capillary chromatographic column of the PLOT type demonstrated that utilization of this type of denuder may be not so straightforward, especially for determining temporary concentrations, keeping in mind the long time required to achieve the equilibrium state.

References

- [1] H. Van Reeuwijk, P.K. Fisher, H. Harssema, D.J. Briggs, K. Smallbone, E. Lebert, *Environ. Monit. Asses.* 50 (1998) 37.
- [2] A. Kasper-Giebl, H. Puxbaum, *Atmos. Environ.* 33 (1999) 1323.
- [3] J. Pawliszyn, *Solid Phase Microextraction. Theory and Practice*, Wiley & Sons Inc, New York, 1997.
- [4] S.P. Thomas, R.R. Sri, G.R.B. Webster, L.P. Sarna, *Environ. Sci. Technol.* 30 (1996) 1521.
- [5] L.E. Ekberg, *Atmos. Environ.* 28 (1994) 3571.
- [6] L.C. Holcomb, *Environ. Int.* 19 (1993) 9.
- [7] Z. Ali, C.L.P. Thomas, J.F. Alder, *Analyst* 114 (1989) 759.
- [8] J. Namiesnik, M. Pilarczyk, *Toxicol. Environ. Chem.* 64 (1997) 203.
- [9] K. Grob, A. Habich, *J. Chromatogr.* 321 (1985) 45.
- [10] D.J. Eatough, F. Obeidi, Y. Pang, Y. Ding, N.L. Eatough, W.E. Wilson, *Atmos. Environ.* 33 (1999) 2835.
- [11] R.J. Rando, H.G. Poovey, *Am. Ind. Hyg. Assoc. J.* 60 (1999) 737.
- [12] M.E. McComb, R.D. Oleschuk, E. Giller, H.D. Gesser, *Talanta* 44 (1997) 2137.
- [13] P.K. Simon, P.R. Dasgupta, *Anal. Chem.* 65 (1993) 1134.
- [14] Z. Zdrahal, Z. Vecera, *J. Chromatogr. A* 668 (1994) 371.
- [15] A. Peskova, P. Parizek, Z. Vecera, *J. Chromatogr. A* 918 (2001) 153.
- [16] B.V. Burger, M. Le Roux, W.J.G. Burger, *J. High Resol. Chromatogr.* 13 (1990) 777.

- [17] S. Blomberg, J. Roeraade, *J. High Resol. Chromatogr.* 13 (1990) 509.
- [18] K.D. Bartle, C.L. Woolley, K.E. Markides, M.L. Lee, R.S. Hansen, *J. High Resol. Chromatogr.* 10 (1987) 128.
- [19] S. Blomberg, J. Roeraade, *J. Chromatogr.* 394 (1987) 443.
- [20] M.S. Krieger, R.A. Hites, *Environ. Sci. Technol.* 26 (1992) 1551.
- [21] M.S. Krieger, R.A. Hites, *Environ. Sci. Technol.* 28 (1994) 1129.
- [22] J. Zheghua, R.E. Majors, E.J. Guthrie, *J. Chromatogr. A* 842 (1999) 115.
- [23] E.T. Zellers, M. Morishita, Q.-Y. Cai, *Sens. Actuat. B* 67 (2000) 244.
- [24] A. Gordin, A. Amirav, *J. Chromatogr. A* 903 (2000) 155.
- [25] C. Aguilar, H.-G. Janssen, C.A. Cramers, *J. Chromatogr. A* 867 (2000) 207.
- [26] H.P. Tuan, H.G. Janssen, C.A. Cramers, *J. Chromatogr. A* 791 (1997) 187.
- [27] V. Camel, M. Caude, *J. Chromatogr. A* 710 (1995) 3.
- [28] W. Janicki, L. Wolska, T. Górecki, J. Namiesnik, *Chem. Anal.* 38 (1993) 432.
- [29] D. Gorlo, L. Wolska, B. Zygmunt, J. Namiesnik, *Talanta* 44 (1997) 1543.
- [30] W. Janicki, L. Wolska, W. Wardencki, B. Zygmunt, *Ochrona Powietrza* 5 (1992) 121.
- [31] P.A. Martos, J. Pawliszyn, *Anal. Chem.* 69 (1997) 206.
- [32] A. Baltussen, F. David, P. Sandra, H.-G. Janssen, C. Cramers, *Anal. Chem.* 71 (1999) 5193.