Ultra thick film open tubular traps with an increased inner diameter

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Abstract

In this paper, the concept of open tubular traps, coated with a very thick film of polydimethyldisiloxane for enrichment of trace volatile components has been further explored. From theoretical calculations as well as practical experiments it is demonstrated that it can be advantageous to increase the inner diameter of such traps. For a given sampling flow rate and phase ratio, the plate number of the traps is not dependent on the inner diameter, provided that the linear flow velocity remains sufficiently high to offset the effect of axial diffusion. It is shown that this is due to the basic fact that for a given sampling flow rate, the average linear flow velocity in the trap is inversely proportional to the square of the inner diameter of the trap. However, in contrast to chromatographic separations, the linear flow velocity is not important. Under conditions of a constant phase ratio, an increased inner diameter also increases the amount of sorbent in the trap, which is a key parameter for obtaining high breakthrough volumes. Open tubular traps with an expanded inner diameter have very low pressure drop characteristics, which provides the possibility to construct new, simplified sampling systems.
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1. Introduction

Analysis of volatile organic compounds at low concentration levels remains a subject of great importance. As regulatory demands become more and more stringent, including revised environmental legislations, tightened quality specification of materials and other, similar issues, there is a need for improved concentration methods in connection with high resolution gas chromatography. In the past, the use of adsorbents has been the dominating methodology for trace enrichment of volatiles [1]. However, during the last decade, the use of sorption technology for analyte concentration has greatly increased [2]. The sorption phases are usually identical to ordinary GC stationary phases, typically polydimethylsiloxane (PDMS). Advantages of sorption enrichment, compared to concentration methods which use adsorbents include

a higher degree of inertness and lower desorption temperatures. Concepts based on sorption are therefore particularly suitable when dealing with reactive and/or thermally labile compounds [3,4].

A sorbent trapping technology, using capillary tubes, coated with an ultra thick film of stationary phase was introduced by us in the 1980s [5,6]. The extremely low phase ratio of such traps and the associated increase of the retention factor (k') of analytes allows a quantitative enrichment of trace volatiles from considerable sample volumes. Since then, the possibilities of the ultra thick film open tubular trap (OTT) concept have been further explored by Burger et al. [7,8] and Rohwer and co-worker [9]. A very popular sorption method is the solid phase microextraction (SPME) technique [10], which is simple to use and has been employed in numerous applications. Other methods are stirbar sorptive extraction (SBSE) [11], packed sorption tubes [12,13] and the large size sorptive probe (LSP) technique [14]. These methods employ a larger amount of sorbent than SPME, which improves their applicability in ultratrace analysis.

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The principle of SPME, SBSE and LSP technologies are based on the establishment of an equilibrium or partial equilibrium between the sorption phase and the analytes in a surrounding sample. The OTT as well as the packed sorption tube technology can be operated in the equilibrium mode or in the breakthrough sampling mode. The advantage of the breakthrough mode is that analyte trapping is quantitative by definition, which simplifies the interpretation of the subsequent GC results.

Open tubes have the feature of an inherently low hydraulic resistance [15] which is also one of the well known fundamental advantages of open tubular (capillary) columns. This makes it easy to optimize the number of theoretical plates for a given flow velocity by increasing the length of the OTT (e.g. to a few meters), while a low pressure drop can be maintained. For packed traps, the significantly higher hydraulic resistance would in such cases lead to an excessive pressure drop. In practical work, only short packed sorption tubes have been used, with poor retention of low boiling analytes [13].

Unfortunately, due to its capillary dimensions, the overall volumetric sampling rate which can be employed with OTTs is quite limited. One way to overcome this problem would be to use a number of tubes in parallel; a concept which has been explored by Rohwer and co-worker [9]. However, these authors used short traps, which, at high flow rates, provide an insufficient number of theoretical plates to ensure quantitative trapping of highly volatile components. A more efficient parallel OTT, based on 120 capillary traps, has been reported by Krieger and Hites [16]. However, the capillaries which were utilized had an inadequate retention power for highly volatile solutes.

Recently, we reported a new procedure for preparation of OTTs, where a PDMS prepolymer is simply forced through a capillary tube by pressurized gas [17]. The resulting wave-like film of prepolymer is then cross-linked in situ by raising the temperature. We showed that the sampling capacity of such OTTs is affected very little in spite of the irregularity of the sorbent film. The coating procedure is extremely straightforward and can be performed in any average laboratory.

In the present paper, we have utilized the new coating technology and extended our study of the OTT concept. The goal was to increase the concentration power for very volatile analytes, for which current sorption-based methods are not particularly suitable. Both in a theoretical discussion as well as in practical experiments, we show that this is possible by *increasing* the inner diameter of OTTs.

2. Theory

The maximum sample volume, at which an analyte breakthrough starts to occur (the breakthrough volume (V_B)) can generally be written as [18]:

$$V_B = V_R f(N, b) \tag{1}$$

where N is the number of theoretical plates of the trap, b is an arbitrary level (%) of tolerable analyte breakthrough and V_R is the retention volume of the trap. Thus, in order to obtain the largest possible breakthrough volume, both the retention volume and the efficiency of the trap should be optimized. The retention volume can be written as:

$$V_R = V_M(k' + 1) \tag{2}$$

Here, V_M is the gas holdup volume of the trap and k' is the retention factor. The retention volume may also be expressed by the relationship $k' = K_D/\beta$, where K_D is the analyte distribution ratio and β is the phase volume ratio defined as $\beta = V_M/V_S$ where V_S is the volume of the sorbent phase:

$$V_R = V_S(K_D + \beta) \tag{3}$$

For ultra thick film traps, the value of β is negligible compared to the value of K_D, which may be 100 or higher, even for very volatile components [5]. Thus, the elution volume as well as the breakthrough volume is *directly proportional* to the volume of the sorbent.

The second term in Eq. (1) expresses the proportion of the elution volume that can be sampled having a certain trap efficiency and for a predefined, acceptable level of analyte loss. For a loss of 5%, this term becomes [18]:

$$f(N, b = 0.05) = \left(0.9025 + \frac{5.360}{N} + \frac{4.603}{N^2} \right)^{-1/2} \tag{4}$$

The efficiency of the trap can be calculated from its length, L, and the plate height, H, using the relationship $N = L/H$. The relationship between the plate height H and the average linear velocity $\bar{u}$, of the sample can be obtained from the Golay equation [19,20]:

$$H = 2D_M \frac{1}{\bar{u}} + \frac{1}{96D_M} \frac{11k'^2 + 6k' + 1}{(k' + 1)^2} d_M^2 \bar{u}$$
$$+ \frac{2}{3D_S} \frac{k'}{(k' + 1)^2} d_f^2 \bar{u} \tag{5}$$

where D_M is diffusion coefficient of the analyte in the gas phase, D_S is the diffusion coefficient in the sorption phase, d_M is the diameter of the non-coated (open) cross section of the trap and d_f is the film thickness of the sorption phase. The expression for plate height may be rewritten in terms of K_D and β instead of k':

$$H = 2D_M \frac{1}{\bar{u}} + \frac{1}{96D_M} \frac{11K_D^2 + 6K_D\beta + \beta^2}{(K_D + \beta)^2} d_M^2 \bar{u}$$
$$+ \frac{2}{3D_S} \frac{K_D\beta}{(K_D + \beta)^2} d_f^2 \bar{u} \tag{6}$$

From a practical perspective, the sampling flow rate is more relevant than the gas velocity inside the trap. Assuming a negligible pressure drop, Eq. (6) can be expressed in terms

of the flow (F), where F is defined as

$$F = \frac{\pi}{4} d_M^2 \bar{u} \qquad (7)$$

This results in

$$H = \frac{\pi D_M}{2} d_M^2 \frac{1}{F} + \frac{1}{24\pi D_M} \frac{11 K_D^2 + 6 K_D \beta + \beta^2}{(K_D + \beta)^2} F$$

$$+ \frac{2}{3\pi D_S} \frac{K_D}{(K_D + \beta)^2} (\sqrt{1 + \beta} - \sqrt{\beta})^2 F \qquad (8)$$

At sufficiently high flow rates (which are employed in practical applications), the first term in Eq. (8) can be neglected. Under such conditions, the plate height is then only dependent on the phase ratio *and not on the diameter of the trap*. In other words, there would be no loss in efficiency if the diameter of the trap is increased, provided that β is kept constant. The limits are only determined by the relative influence of longitudinal diffusion, which becomes significant when the flow velocity in the trap becomes very low. The theory also predicts that the independence of plate height on inner diameter is true not only for OTT's but also for open tubular chromatography columns. At first sight, this conclusion looks controversial, but the results should be interpreted in terms of the fundamental differences between sample trapping and chromatography. An increased inner diameter for a given flow rate will reduce the linear gas velocity in the trap/column by a square factor as shown in Eq. (7). For chromatographic separations, this would be devastating in terms of analysis time, and therefore this is not a realistic option. For sample enrichment/trapping, linear gas velocity in the trap is of no importance, since the analytes are not eluted. Only the volumetric flow rate determines the time frame, in which analytes in a certain sample volume can be concentrated.

From Eqs. (1), (3), (4) and (8), the breakthrough volumes of OTTs with different diameters can be calculated. Fig. 1 shows the simulated V_B as a function of the flow rate for three traps with different inner diameters. In this simulation, all traps were assumed to have the same length (200 cm) and a β-value of 1. A K_D of 200 was chosen, which is a typical value for a component such as hexane [5], while the diffusion coefficients in the mobile phase and the stationary phase were in accordance with data obtained from literature [21,22]. As can be seen from the figure, the trap with the largest inner diameter (4.5 mm) has clearly the largest breakthrough volume, even for flow rates of 100 ml/min. At lower flow rates, the adverse effect of longitudinal diffusion starts to become important. This is strongly diameter-dependent as can be seen from the expanded (left) part of Fig. 1. For the 4.5 mm i.d. trap, the breakthrough volume starts to deteriorate at a flow rate of 0.5 ml/min, but not for the traps with smaller i.d.s.

In practice, much higher flow rates are utilized, and theoretically, the inner diameter of the trap can be increased to extremely large values, before an appreciable deterioration
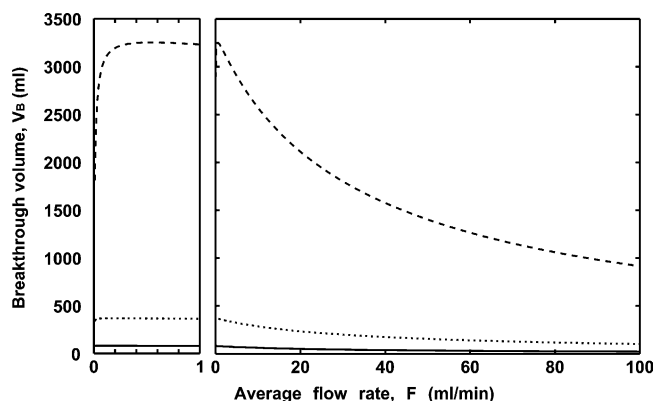

Fig. 1. Calculated breakthrough volume V_B (ml) vs. average flow F (ml/min) for three different traps. All traps have a length of $L = 200$ cm and a phase ratio $\beta = 1$. The partition ratio $K_D = 200$. The diffusion coefficient in mobile phase $D_M = 7 \times 10^{-2}$ cm²/s and the diffusion in the sorbent (PDMS) $D_S = 3 \times 10^{-6}$ cm²/s. The solid curve (—), the dotted curve (······) and the dashed curve (– – –) correspond to data for traps with inner diameters of 700, 1500 and 4500 μm, respectively. The corresponding volume of sorbent in these traps is 0.385, 1.77 and 15.9 ml.

of the plate height is encountered. This is illustrated in Fig. 2 where the plate height is shown as a function of the inner diameter of the OTT. For a flow rate of 100 ml/min, the increase in plate height is marginal even for an OTT with an inner diameter of 10 cm! As an effect of the increased amount of sorbent, the breakthrough volume, as a function of inner diameter continues to increase until the effects of longitudinal diffusion start to counterbalance this increase. This is shown in Fig. 3. V_B reaches a maximum value in the form of an asymptote and there is therefore no distinct optimum inner diameter.
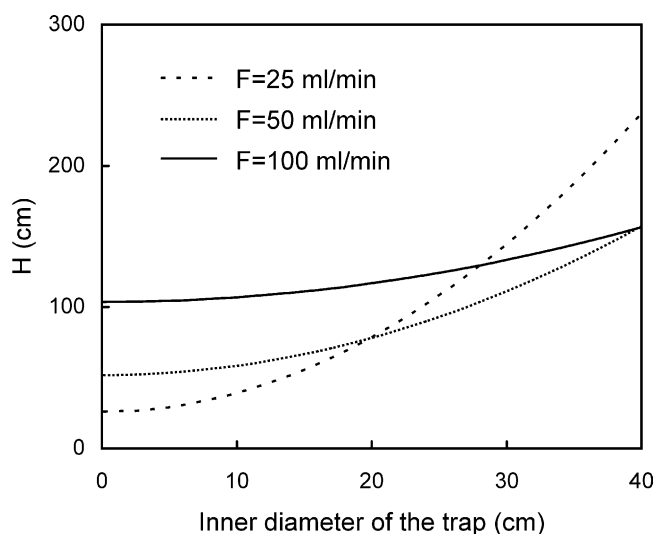

Fig. 2. The theoretical plate height for three different flow rates, as a function of the inner diameter of the trap. Phase ratio (β) = 1, partition ratio (K_D) = 200.
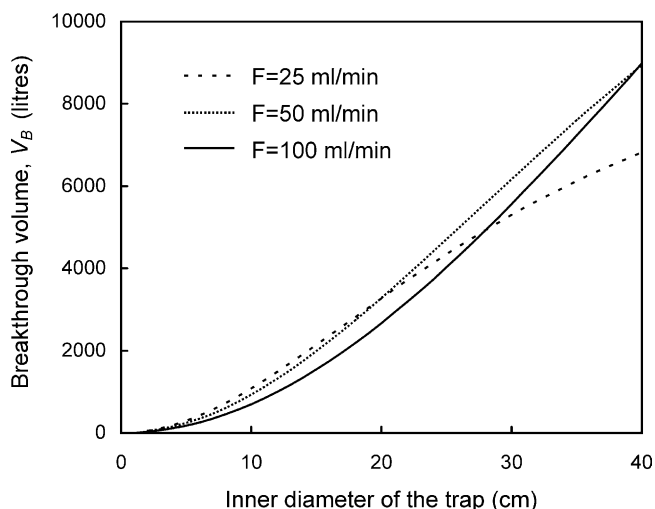
Fig. 3. The calculated breakthrough volume as a function of the inner diameter of the trap, for three different flow rates. Trap length: 200 cm, phase ratio (β) = 1, partition ratio (K_D) = 200.

3. Experimental

3.1. Open tubular thick film traps

Three open tubular traps, all coated with PDMS, using the prepolymer SYLGARD® 184 (Dow Corning, USA), were utilized in a practical performance comparison. All traps were coiled (coil diameter of 10 cm), with both ends left straight (about 7 cm each) to facilitate their mounting during coating and in instruments used during the subsequent measurements.

The first trap (#1) was a borosilicate capillary, coated with a smooth, regular PDMS film, according to a process, described by Blomberg and Roeraade [6]. The second trap (#2, Silcosteel® capillary tube, Restek Corp., USA) and the third trap (#3, borosilicate tubing), were coated with an irregular film of PDMS according to a new procedure. This coating technique has recently been described in detail [17]. In short, the tube which was placed in a GC oven, was completely filled with the prepolymer fluid from a pressurized vial. Subsequently, the bulk of the prepolymer was blown out of the tube by additional pressurization. This resulted in the formation of an irregular film of prepolymer on the inner wall of the tube. This film was polymerized by quickly raising the temperature of the oven to 200 °C. The polymer was then further cured for 15 min under gas flow (nitrogen). The dimensions of the final average film thickness of the sorbent layer can be controlled by partially pre-curing the prepolymer at elevated temperature and by the pressure, applied to remove the excess of prepolymer. The average film thickness of the traps was determined gravimetrically. The specifications of the traps are listed in Table 1.

3.2. Instrumental

Evaluation of the retention performance and efficiency of the traps was carried out on a 6890GC (Agilent Technologies,

Table 1
Properties of the prepared traps

	Trap #1	Trap #2	Trap #3
Length (cm)	155	400	309
Tube i.d. (mm)	0.718	0.762	1.53
Average film thickness (μm)	91	105.5	215
Stationary phase volume (ml)	0.28	0.87	2.74
β	1.26	1.10	1.07

CA, USA) with a split injector (100 °C) and a flame ionization detector. The GC oven temperature was kept at 27 °C. Nitrogen was used as carrier gas. The traps were connected to the injector and detector via stainless steel connectors in each end (ZRU1.5, VICI AG, Switzerland or SS-200-6-1, Swagelok, OH, USA (for trap #3)) followed by a short piece of deactivated fused silica tubing (length: ca. 20 cm, 320 μm i.d., Agilent Technologies). The elution analyses were performed by injecting 20 μl of hexane headspace using an autoinjector (G1513A, Agilent Technologies) and a gas tight syringe (50 μl, Agilent Technologies). Frontal analyses were performed as shown schematically in Fig. 4. A constant flux of hexane was delivered by a diffusion-based setup [21]. A 5 ml septum-capped glass vial containing 0.5 ml of the hexane, including a short length of fused silica capillary tubing (3 cm, 320 μm i.d.) pierced through the septum of the vial, was mounted inside a stainless steel container (60 ml). A flow of carrier gas (nitrogen), regulated by a needle valve (SS-SS2-D, Swagelok) was passed through the container and a capillary transfer line (50 μm i.d., 3 dm, fused silica), which was further connected to the GC injector (pierced through the injector septum). In this way, a constant flux of hexane vapor was introduced into the injector. This vapor was further diluted by additional carrier gas, since the injector was operated in split mode at a split ratio of 1:3.
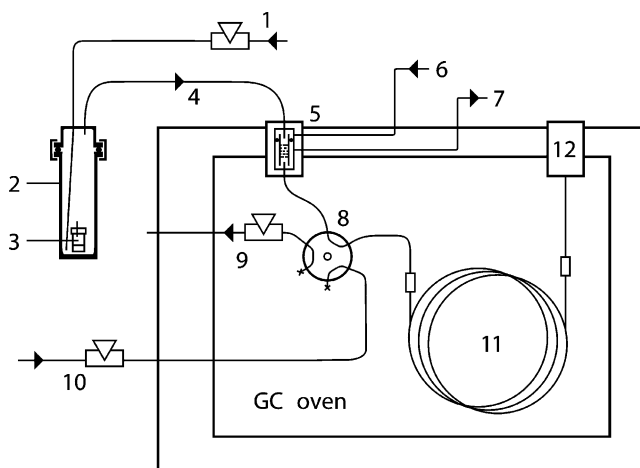

Fig. 4. A schematic of the setup used for the frontal analysis. The valve setting of the system is shown in the analysis mode. 1: carrier gas supply, regulated with a needle valve, 2: stainless steel container, 3: vial containing hexane, 4: fused silica transfer line, 5: split injector, 6: carrier gas supply to splitter, 7: split-line (split ratio 1:3), 8: 6-port switching valve, 9: needle valve, 10: carrier gas supply, regulated with a needle valve, 11: thick film trap to be evaluated, 12: flame ionization detector.

An air-actuated 6-port valve (A4C6WT, VICI AG) was mounted between the injector and the trap, which allowed switching from a needle valve-controlled auxiliary carrier gas supply (initial position), to the flow of hexane vapor (analysis position).

The frontal analysis was performed by first adjusting needle valve (1), with the 6-port valve in the analysis position, until a reasonable and stable signal from the FID was obtained. Then, the 6-port valve was switched, which purged the trap with pure carrier gas delivered via needle valve (10) in foreflush direction. Meanwhile, the flow rate of the hexane vapor, passing via the other needle valve (9) was adjusted to the same value as the flow through the trap in the analysis position. This eliminated disturbances in the analyte profile, related to flow switching. To start the frontal analysis, the 6-port valve was switched again, now introducing a constant flux of hexane vapor with a sharp leading band profile.

Statistical moments of the peaks were calculated using Chemstation software (Agilent Technologies). Theoretical calculations were performed using the software Matlab®, version 6.5 (The MathWorks Inc., Natick, MA, USA).

4. Results and discussion

In order to validate our theoretical conclusions from above, a series of elution analyses at different gas velocities with hexane as solute were performed. The study included the two traps with different diameters and irregular coatings, specified in Table 1 as well as an OTT with a smooth, regular coating. To obtain an accurate peak characterization, statistical moments were employed [23]. The number of theoretical plates (N) was calculated using Eq. (9).

$$N = \frac{M_1^2}{M_2} \tag{9}$$

where M_1 is the first moment, the elution time of the centre of gravity of the peak(s) and M_2 is the second central moment, the variance of the peak(s^2).

The H versus the average flow rate (F) was calculated for each trap, and the results are shown in Fig. 5. According to the theoretical considerations discussed above, the slope of these curves should only depend on the β-value. The two traps coated with an irregular film of sorbent do approximately have the same average β-value and their H/F characteristics are indeed very similar. The trap with the smooth coating of sorbent displays somewhat lower plate heights. This is probably related to the slightly higher β-value of this trap. An additional reason could be the absence of film irregularity.

The breakthrough volumes (5% level of breakthrough) of the traps were calculated by applying Eqs. (1), (4) and (9), using the experimental data of V_R and N for hexane, obtained from the elution analysis. The results are shown in Fig. 6 as plotted values. It should be noted that the traps have different length, and therefore the breakthrough data are not directly
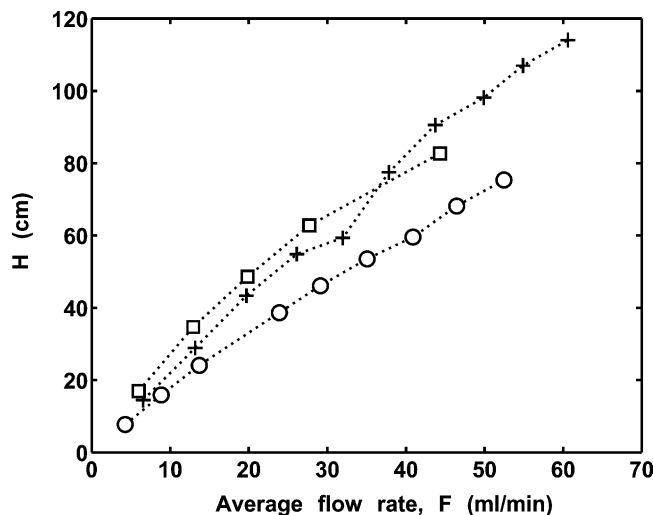

Fig. 5. Plate height vs. average flow rate for the three traps listed in Table 1, where hexane was used as the test solute. The ($\bigcirc$) values are for the reference trap (#1). The crosses (+) correspond to trap #2 and the squares ($\square$) belong to trap #3.

comparable. Trap #1 with the smooth film of sorbent had a length of only 155 cm and was included mainly as a reference. Trap #2 had a length of 400 cm and an inner diameter of 0.762 mm. Trap #3, having the largest inner diameter (1.53 mm) has a significantly higher breakthrough volume, in spite of the fact that its length is only 309 cm. On this trap, concentration of hexane is quantitative from a sample volume of more than 300 ml, at a flow rate of 50 ml/min.

Frontal analysis was also performed with this trap to validate the breakthrough curve obtained by the elution analysis. The frontal breakthrough volumes were calculated using
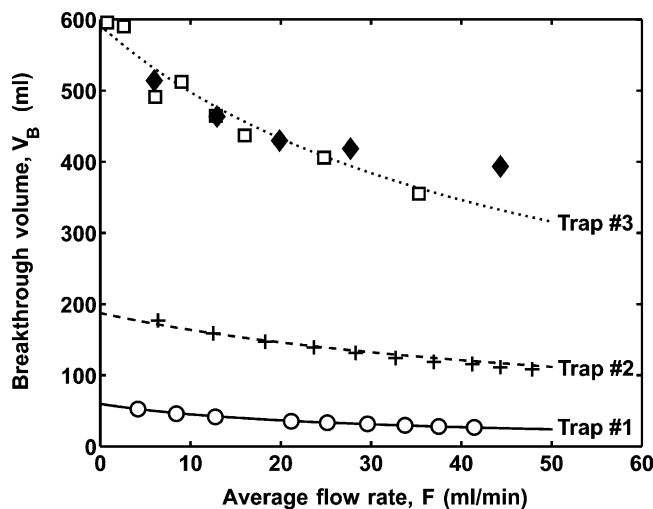

Fig. 6. Breakthrough volume for hexane plotted vs. average flow for the three traps listed in Table 1. The ($\bigcirc$) values are for the reference trap (#1). The squares ($\square$) and diamonds ($\blacklozenge$) are breakthrough volumes determined by frontal analysis and elution analysis respectively. The solid curve (—) corresponds to the theoretical values fitted to the partition ratio, phase volume ratio and diffusion coefficients of trap #1. The dashed curve (– – –) and the dotted curve (······) are the theoretical values, scaled to fit the dimensions of trap #2 and trap #3.

Eq. (10) [18].

$$b = \frac{\int_0^t I(t)\, dt}{I_{EQ}t\, dt} \tag{10}$$

where $I(t)$ is the the frontal shape of the baseline corrected detector signal, which was numerically integrated. At the low analyte concentrations used, this signal will be proportional to the mass flux from the trap. I_{EQ} is the baseline corrected FID signal at equilibrium sampling, obtained after a prolonged sampling time. As can be noted from Fig. 6, there is a good correspondence between the values obtained from the frontal and the elution analysis.

At this stage, we were interested to know how these practical results would correlate with our theoretical predictions, particularly with respect to the beneficial effect of an increased trap diameter. For this purpose, the values of K_D and D_S need to be known. However, the available literature data may not be applicable to our system due to, e.g. differences in sorbent properties. Therefore, these constants were determined from the elution analysis data, obtained with the smooth-film trap. First, the average K_D-value was calculated from the elution volume and the known volumes of stationary and mobile phase. Accordingly, K_D for hexane was found to be 203.9 ± 1.6. In order to determine D_S, the least square method was employed, where Eq. (8) was loaded with the experimental plate height versus flow rate data (shown in Fig. 5). The value for D_M (6.8 × 10^{-2} cm²/s) was retrieved from literature [21], and can be assumed to be applicable in our system. Solving Eq. (8) resulted in a D_S-value of 1.4×10^{-6} cm²/s, which seems reasonable.

Using these K_D and D_S values, as well as the experimentally determined V_S and V_M of each trap, the theoretical breakthrough volumes were calculated for the two traps with larger inner diameters. The results are reported in Fig. 6 in the form of line graphs, (shown together with the plotted experimental values), which demonstrates the excellent correlation between our theoretical model and the experimental data.

Some additional conclusions regarding the thick film (low phase ratio) trap concept can be made from Eq. (8). D_M, in the second term of the equation, is roughly four orders of magnitude larger than D_S, but the magnitude of this term is also very much dependent on the partition ratio. For analytes with a large K_D, (e.g. 10,000, which is roughly the K_D-range of decane), the second term in the equation will therefore represent the main contribution to plate height. Since $K_D \gg \beta$, the equation can be simplified as:

$$H = \frac{11}{24\pi D_M} F \tag{11}$$

Thus, for high boiling analytes, the plate height for a given flow becomes independent of the film thickness of sorbent and partition ratio of the analyte.

When dealing with low boiling analytes (partition ratio 50–300), the third term in Eq. (8) becomes very large and will
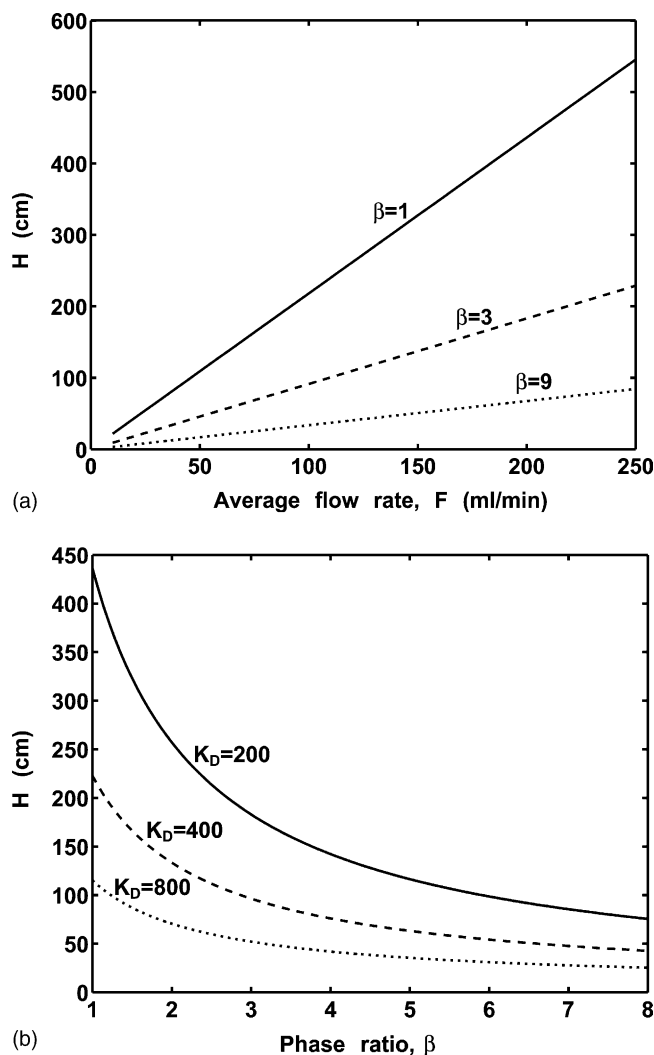

Fig. 7. (a) Calculated plate height vs. average flow rate for three open tubular traps with different phase ratios. The partition coefficient (K_D) = 200. (b) Calculated plate height for analytes with different partition ratios, using an open tubular trap and a flow rate of 200 ml/min. In both (a) and (b), the values for D_M and D_S are 6.8×10^{-2} and 1.4×10^{-6} cm²/s, respectively.

now represent the main contribution to plate height. However, K_D is still $\gg \beta$. The plate height for low boiling analytes can thus be simplified and rewritten as:

$$H = \frac{2}{3\pi D_S} \frac{1}{K_D} \left(\sqrt{1+\beta} - \sqrt{\beta}\right)^2 F \tag{12}$$

For volatile compounds, H is thus considerably dependent on both the phase ratio and the partition ratio. This dependence is further shown in Fig. 7a. From these graphs it can be seen that sampling at high flow rates requires a significant increase of β, otherwise the plate height becomes prohibitively high. But in order to maintain a given breakthrough volume, the sorbent volume cannot be reduced. The column diameter should therefore be *increased*. The situation is much less critical for solutes with higher partition ratios (Fig. 7b).

Finally, some other aspects of OTTs with an increased diameter should be mentioned. First, the pressure drop of such traps decreases dramatically which means that very simple sampling systems, even without pumps, can be designed, including "self-driven" systems using, e.g. wind power, or blowing through the trap with "lung power", e.g. for sampling of volatile trace components from alveolar air. Second, while the increased amount of sorbent in large diameter traps is decisive for the increased breakthrough volume, this will also lead to a proportional increase in background from breakdown products of the sorbent. Volatile analytes can be desorbed already at very moderate temperatures, so for this type of components, the background is not likely to become significant.

A very simple oven can be employed for thermal desorption, since an exact temperature control is not required. The low desorption temperature and the inertness of PDMS should allow the concentration and quantitative determination of trace amounts of reactive volatile components, such as low boiling unsaturated aldehydes, isocyanates, amines, etc., for which current analytical techniques are shortcoming.

5. Conclusions

Open tubular traps, coated with a very thick film of sorbent are a useful tool for quantitative concentration of trace volatiles in gases (e.g. air). The sampling volume (in terms of breakthrough volume) of such traps is directly dependent on the amount of sorbent, present in the trap. However, a certain number of theoretical plates are also required; otherwise the sampling capacity becomes too low. Both objectives can be achieved by increasing the inner diameter of open tubular traps. For a given flow rate and phase ratio, the number of theoretical plates is *independent* on the inner diameter. This is due to the basic fact that for a given sampling flow rate, the average linear flow velocity in the trap is inversely proportional to the square of the inner diameter of the trap. In contrast to chromatographic separations, a decreased linear flow velocity is not important until the influence of longitudinal diffusion becomes appreciable. When reasonably large sampling flow rates are employed, this does not become a problem, even when the diameter of the OTT is very large. The limits of traps with an increased inner diameter are more related to practical issues like the degree of chemical background generated by the sorbent and the stage where thermal desorption and cryofocusing of the analytes becomes technically incompatible with the void volume of the trap.

It is anticipated that thick film open tubular traps with a large inner diameter are particularly suitable for concentration of very volatile analytes, including reactive and thermolabile trace components.

References

[1] V. Camel, M. Caude, J. Chromatogr. A 710 (1995) 3.
[2] E. Baltussen, C.A. Cramers, P.J.F. Sandra, Anal. Bioanal. Chem. 373 (2002) 3.
[3] E. Baltussen, F. David, P. Sandra, H.-G. Janssen, C. Cramers, Anal. Chem. 71 (1999) 5193.
[4] E. Baltussen, F. David, P. Sandra, C. Cramers, J. Chromatogr. A 864 (1999) 345.
[5] S. Blomberg, J. Roeraade, J. Chromatogr. 394 (1987) 443.
[6] S. Blomberg, J. Roeraade, HRC & CC 11 (1988) 457.
[7] B.V. Burger, M. Le Roux, W.J.G. Burger, J. High Resolut. Chromatogr. 13 (1990) 777.
[8] B.V. Burger, M. Le Roux, Z.M. Munro, M.E. Wilken, J. Chromatogr. 552 (1991) 137.
[9] E.K. Ortner, E.R. Rohwer, J. High Resolut. Chromatogr. 19 (1996) 339.
[10] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[11] E. Baltussen, P. Sandra, F. David, C. Cramers, J. Microcol. Sep. 11 (1999) 737.
[12] E. Baltussen, H.G. Janssen, P. Sandra, C.A. Cramers, J. High Resolut. Chromatogr. 20 (1997) 385.
[13] E. Baltussen, F. David, P. Sandra, H.-G. Janssen, C.A. Cramers, J. High Resolut. Chromatogr. 21 (1998) 332.
[14] J. Pettersson, A. Kloskowski, C. Zaniol, J. Roeraade, J. Chromatogr. A 1033 (2004) 339.
[15] G. Guiochon, Anal. Chem. 50 (1978) 1812.
[16] M.S. Krieger, R.A. Hites, Environ. Sci. Technol. 26 (1992) 1551.
[17] A. Kloskowski, J. Pettersson, J. Roeraade, J. Chromatogr. A 1035 (2004) 159.
[18] P. Lövkvist, J.Å. Jönsson, Anal. Chem. 59 (1987) 818.
[19] L.S. Ettre, Open Tubular Columns in Gas Chromatography, Plenum Press, New York, 1965.
[20] M.J.E. Golay, in: D.H. Desty (Ed.), Gas Chromatography, Butterworth, 1958, p. 36.
[21] M. Gautrois, R. Koppmann, J. Chromatogr. A 848 (1999) 239.
[22] J. Dewulf, H. Van Langenhove, M. Everaert, J. Chromatogr. A 761 (1997) 205.
[23] J.P. Foley, J.G. Dorsey, Anal. Chem. 55 (1983) 730.