ELSEVIER

Journal of Chromatography A, 863 (1999) 57–68

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Trapping efficiency of aqueous pollutants in multichannel thick-film silicone-rubber traps for capillary gas chromatography ☆

E.K. Ortner, E.R. Rohwer*

Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa

Received 13 September 1998; received in revised form 14 July 1999; accepted 21 July 1999

Abstract

Established standard methods for analysing aqueous pollutants by capillary gas chromatography are cumbersome, time-consuming and expensive. With the aim of replacing the sample preparation procedures with direct concentrating and thermal desorption steps multichannel silicone-rubber traps were tested to determine breakthrough volumes and optimum accumulation conditions as a function of water flow-rate. Larger multichannel traps, consisting of 32 silicone tubes in parallel were made to increase the collection flow-rate through the trap with the same extraction efficiency of the initial smaller traps. It was shown that by increasing the number of parallel silicone tubes in the multichannel trap the breakthrough volume of benzene is 37 ml at a flow-rate of 75 μl/min and the trap displays 11 theoretical plates under these conditions.

Keywords: Extraction methods; Water analysis; Phenol; Benzene

1. Introduction

The analysis of water contaminants with very low concentrations of compounds (i.e., 0.02–200 μg/l) is a complex problem which can so far only be solved by using isolation and preconcentration procedures prior to gas chromatographic analysis. These isolation techniques can be divided into the following basic groups: liquid–liquid extraction; gas extraction; sorption from water; permeation techniques; and other methods. Sorption extraction has developed as a largely empirical method of sample preparation. Sorption extraction techniques are divided into two main groups; solid-phase extraction (SPE) and open tubular trapping (OTT). OTT is very similar to SPE, except that water samples are passed through open tubular thick-film silicone-rubber traps instead of packed bed cartridges or disks. Also with OTT the retention of the analytes from water is based on the analytes partitioning into the stationary phase rather than adsorption of the analytes on the surface of the stationary phase. The sorbent material used in OTT is very similar to the fibre of a solid-phase microextraction (SPME) device [1], which is introduced directly into the water sample whereupon the analytes diffuse into the fibre until equilibrium is established. Subsequently the analytes are desorbed thermally from the SPME fibre in the gas chromatographic injector. OTT is different from SPME in that it is not a single equilibrium method, but rather the

☆Presented at the 22nd International Symposium on Chromatography, Rome, 13–18 September 1998.

*Corresponding author. Tel.: +27-12-4202-518; fax: +27-12-3625-297.

E-mail address: erohwer@scientia.up.ac.az (E.R. Rohwer)

0021-9673/99/$ – see front matter
PII: S0021-9673(99)00845-6

analyte molecules move through the trap by a normal chromatographic process which results in complete extraction before the onset of breakthrough. The micro pollutants from OTT can either be thermally desorbed with cryogenic refocusing or solvent extracted with a small volume of a suitable solvent. Like SPME, OTT can thus be a solventless water analysis technique.

Initially, thick-film silicone-rubber traps consisted of a glass capillary column [2–4] or a silica tube filled with a silicone-rubber tube [5]. These traps show acceptable retention, low resistance to water flow and are suitable for repetitive collection of water samples. To provide acceptable retention capacities, long traps are manufactured. The low sampling flow-rates needed to prevent immediate breakthrough of the analytes in single channel traps inspired the development of deformed open-tubular extraction columns (e.g., coiling, stitching, weaving) [6]. We decided to rather increase the capacity of the thick-film traps by changing their configuration to a shorter more manageable multichannel trap, consisting of a silica tube filled with a few silicone-rubber tubes positioned in parallel.

Recently Baltussen and co-workers have prepared a packed bed trap from crushed silicone-rubber tubes, obtaining exciting results for air [7] and water [8,9] samples. At present this is the sorption trap in the literature which is the most similar to our multichannel silicone-rubber trap.

In our previous article [10] it was shown that organic compounds can easily and reproducibly be extracted from water samples with the multichannel silicone-rubber trap and analysed by gas chromatography (GC). However it is also necessary to characterise the kinetic trapping efficiency of a sorption trap. With a water sample of unknown concentration it is important to know the breakthrough volume of a sorption trap at varying flow-rates, to ensure complete extraction of the compounds. Also, if the range of concentration is known (i.e., ppb or ppt) and the breakthrough volumes are available for a sorption trap, it is possible to determine the highest flow-rate that still allows complete extraction of the sample in order to save time.

For comparison between the extraction efficiency of different types of sorption traps it is necessary to know the number of theoretical plates of a trap under specific conditions. Additionally one should compare traps by their capacity factor (k) for a specific compound. The capacity factor can experimentally be determined using the following equation [11]:

$$k = \frac{V_R}{V_0} - 1 \quad (1)$$

where V_R is the retention volume of a specific compound and V_0 is the hold up volume of the trap. The capacity factor is of course independent of the extraction flow-rate, as V_0 is constant for a specific trap and V_R is independent of the flow-rate used.

In this study we will look at the kinetic parameters of the multichannel trap for the direct analysis of water samples, by determining the number of theoretical plates and breakthrough volumes of specific compounds as a function of flow-rate and trap configuration. The capacity factors for some organic compounds extracted from water with the multichannel silicone-rubber trap are also determined. Preconcentration of a sample onto a trap is different from ordinary analytical gas and liquid chromatography in several respects: the sample enters the column as a front instead of a narrow plug; as no separation is intended, it is not necessary to have as many theoretical plates as for an analytical column; the retention must be large, in order to permit large sample volumes. Due to the unconventional configuration of the multichannel trap, band broadening cannot simply be calculated with theoretical models developed for open tubular or packed columns. As a result, different techniques for the experimental determination of plate numbers and breakthrough volumes were studied.

2. Theory

Experimentally there are two techniques: (1) elution analysis and (2) frontal analysis, which can be used to determine the number of plates of a trap and the breakthrough volumes of a compound. With elution analysis a plug of standard is injected onto the top of the trap and then water is passed through the trap until a chromatographic peak is obtained. With frontal analysis an aqueous standard is passed through the trap until a S-curve is obtained (see Fig. 1). The S-curve is obtained with initially no break-

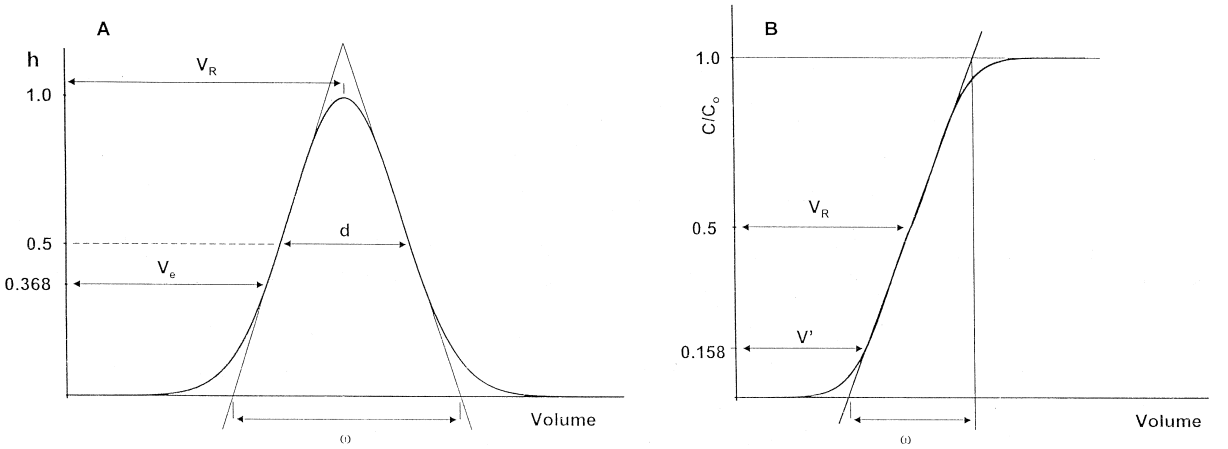

Fig. 1. Diagrammatic representation of an (A) elution analysis curve and (B) frontal analysis curve. Both curves indicate the parameters used for the experimental determination of N and V_b.

through, then slowly breakthrough occurs producing the slope of the curve and finally there is total breakthrough at the flat top part of the curve. When total breakthrough occurs, the quantity of standard that enters the trap is equal to that leaving the trap and therefore the quantity of standard in the trap is constant from this volume onwards.

2.1. Determination of the number of theoretical plates

There are several methods in the literature to determine the theoretical number of plates, as well as breakthrough volumes of a trap from elution and frontal curves. Depending on the peak shape that is obtained from an elution analysis experiment, the method of theoretical plate determination will vary. The most general and widely applied equation to determine the theoretical plate number, N, for a chromatographic column is

$$N = \left(\frac{V_R}{\sigma}\right)^2 \tag{2}$$

where V_R is the retention volume and σ is the standard deviation (in volume units). If a peak is Gaussian, σ is simply measured as the width of the peak at 0.882 of maximum peak height.

For columns with low plate numbers, which elute asymmetrical peaks, Purnell [16] suggests that more accurate calculations from experimental data will be obtained using

$$N = 5.545\left(\frac{V_R V_e}{d^2}\right) \tag{3}$$

where V_e is the volume at 0.368 height of the leading edge of the peak and d is the width of the peak at half height (see Fig. 1).

Said [23] derives that for asymmetrical peaks that are described by the Poisson distribution the number of theoretical plates can be determined with

$$N = 16\left(\frac{V_R}{\omega}\right)^2 \tag{4}$$

where ω is the base width of the peak between the peak tangents.

With asymmetrical peaks all these above equations could still initiate an error in the calculation of the theoretical plate number and possibly a more accurate calculation method of the theoretical plate number is with the use of statistical moments. Functionally, a chromatographic peak is simply a time distribution of the chromatographic height $h(t)$ at any retention time, t. The statistical moments of the peak are mathematically defined as [12–15]: the zeroth-order,

$$M_0 = \int_0^\infty h(t)\mathrm{d}t \tag{5}$$

the first-order,

$$M_1 = \frac{\int_0^\infty th(t)\mathrm{d}t}{M_0} \quad (6)$$

and the higher-order central moments,

$$M_n = \frac{\int_0^\infty (t - M_1)^n h(t)\mathrm{d}t}{M_0} \quad (7)$$

where $n = 2,3,4 \ldots ...$

The first moment (M_1) corresponds to the elution time of the centre of gravity of the peak, since it is obtained by weighting the elution time of each point in the peak by its concentration. Higher moments are more usefully defined as central moments, obtained from the distribution of the peak around the first moment. The second central moment (M_2) is the variance (the square of the standard deviation of the peak). This is the parameter used to calculate the plate number of a column,

$$N = \frac{M_1^2}{M_2} \quad (8)$$

From the third and fourth moment the peak asymmetry (skew) and the extent of vertical flattening (excess) can be calculated. For a Gaussian distribution, statistical moments higher than the second moment have a value of zero. A positive value for the skew indicates a tailing peak. A positive value for the excess indicates a sharpening of the peak profile relative to a Gaussian peak, while a negative value indicates a relative flattening of the upper portions of the peak profile.

Determining the number of theoretical plates from a frontal analysis curve is often related to an elution curve. Raymond and Guiochon [11] make a direct analogy between elution and frontal analysis. They deduce that the number of theoretical plates for both elution and frontal analysis curves is given by the equation:

$$N = 16\left(\frac{V_R}{\omega}\right)^2 \quad (9)$$

where V_R is the retention volume (volume at 2 height on the S-curve) and ω is the base width of the peak and frontal elution curve (measured in volume units) as shown in Fig. 1.

Purnell [16] on the other hand shows that frontal development involves only what corresponds to the leading edge of an elution peak which is almost always sharper than the tailing edge. With the S-curve obtained in frontal analysis the y-axis is a measure of the ratio between the concentration of solute leaving the end of a column (or trap), C, and the initial concentration of solute that entered the column, C_0. For columns with low numbers of plates Purnell shows that the plate number for a frontal analysis curve can be calculated as follows

$$N = \frac{V'V_R}{(V_R - V')^2} \quad (10)$$

where V' is the volume corresponding to the point on the curve where $C/C_0 = 0.1587$ (see Fig. 1).

Said [23] and Reilley et al. [17] show that for frontal analysis the number of plates can be determined by:

$$N = 2\pi\left(\frac{V_{1/2}}{\omega}\right)^2 \quad (11)$$

where $V_{1/2}$ is the elution volume at half height on the S-curve and ω is the distance between the intercepts of the tangents at the points of inflection (see Fig. 1).

2.2. Determination of breakthrough volume

If the number of theoretical plates is known there are a number of ways of determining the breakthrough volume of a compound for a specific trap. In the literature there are three different definitions and methods to determine the breakthrough volume of a compound.

Raymond and Guiochon [11] describe the breakthrough volume of a compound as the retention volume less half the base width of the elution analysis peak for that compound [$V_b = V_R - (\omega/2)$]. Combining this equation with Eq. (9) they obtain the following equation to determine the breakthrough volume, V_b, as a function of retention volume, V_R, and number of theoretical plates, N:

$$V_b = V_R\left(1 - \frac{2}{\sqrt{N}}\right) \quad (12)$$

Lövkvist and Jönsson [18] derived from frontal analysis curves an explicit expression for the breakthrough volume as a function of retention volume and plate number for sampling traps with very low plate numbers

$$V_b = V_R\left(a_0 + \frac{a_1}{N} + \frac{a_2}{N^2}\right)^{-1/2} \quad (13)$$

The parameter a_0 is equal to $(1-b)^2$, which gives the correct asymptotic limit for large values of N. a_2 Was introduced for cases when N tends towards zero and a_1 was used to provide a good fit for intermediate values of N. b Is the breakthrough level and is defined as the fraction of the total mass of analyte which has passed out of the trap and consequently is lost. The parameters a_1 and a_2 are complicated functions of b and their numerical values are given in Table 1 for various values of b. The maximum deviation for V_b between Eq. (13) and the exact solution, obtained by integrating the flux (concentration) at the column inlet and outlet respectively, when N varies from zero to infinity is also given in Table 1.

Mol et al. [19] indicated that from Gaussian elution curves the breakthrough volume of a component in a trapping column is given by the following equation:

$$V_b = V_0(1+k)\left(1 - \frac{3}{\sqrt{N}}\right) \quad (14)$$

where V_0 is the void volume of the trapping column, k the capacity factor of the solute in the trap and N the plate number, with $N>9$. Under conditions where there is a one-sided loss of only 0.15% of the area of a Gaussian-shaped band, the breakthrough volume is defined as $V_R - 3\sigma_v$, where σ_v is the standard deviation of the Gaussian peak eluting from the trapping column. When higher losses are tolerated, Mol et al. [19] show that the breakthrough volume can be redefined, as shown in Table 2.

Table 1
Coefficients in Eq. (13) for different values of the breakthrough level b where max dev. % is the maximum deviation of V_b between Eq. (13) and the exact solution [18]

b, %	a_0	a_1	a_2	Max dev. %
0.1	0.998	29.12	57.54	7
1	0.9801	13.59	17.6	4.4
2	0.9604	9.686	10.69	3.3
5	0.9025	5.36	4.603	1.6
10	0.81	2.878	1.941	0.8

Table 2
Different definitions of breakthrough volume at various breakthrough levels [19]

Breakthrough volume	Equation	Loss (%)[a]
$V_b = V_R - 3\sigma$	(15)	0.15
$V_b = V_R - 2.326\sigma$	(16)	1.0
$V_b = V_R - 1.960\sigma$	(17)	2.5
$V_b = V_R - 1.645\sigma$	(18)	5.0
$V_b = V_R - 1.28\sigma$	(19)	10.0

[a] One-sided loss for a Gaussian-shaped band. Note the different way of expressing the maximum allowable breakthrough compared to Eq. (13), see text.

3. Experimental

3.1. Collection and analysis of standards

Stock standards were made from analytically pure compounds using dichloromethane and methanol as solvents. Distilled–deionised Millipore water was used to make aqueous standards.

Aqueous standards are concentrated on multichannel silicone-rubber traps consisting of eight (MC8) or 32 (MC32) polysiloxane rubber tubes (0.65 mm O.D.×0.30 mm I.D., silastic, medical-grade tubing, Dow Corning, Midlands, MI, USA), placed parallel in a 105×2 mm I.D. and 90×4 mm I.D. silica tube, respectively. The production and conditioning of these traps are described in an earlier article [20].

Breakthrough volume experiments were carried out by injecting 10 μl of the stock standard of phenol or benzene, with concentrations of 0.025 g/ml and 0.175 g/ml respectively, directly onto the multichannel trap and then passing water through the trap to obtain an elution analysis curve. For frontal analysis curves aqueous standards consisting of either phenol or benzene, with concentrations of 330 μg/ml and 175 μg/ml, respectively, were passed separately through the trap. Prior to the addition of stock or aqueous standard to the trap, boiled Millipore water was passed through the trap to remove any air bubbles which could effect the flow of standard through the trap. The trap filled with water was

allowed to cool to room temperature before the standard was passed through the trap. The water standard was allowed to pass through the trap by gravity as described in our previous article [10]. The elution of the standard through the trap was monitored with a UV detector coupled to a Chromperfect data system.

For the determination of the breakthrough volumes of the more hydrophobic compounds, a water standard consisting of a mixture of compounds (naphthalene, acenaphthene, fluorene, pyrene and chrysene) with a concentration of 0.01 μg/ml for each compound, was passed through two MC8 traps in series. The baseline stability of the UV detector did not allow for the accurate monitoring of the very flat S-shaped frontal analysis curves of these well retained compounds. To expand our studies to compounds with high k values, a backup trap was coupled to the exit of the accumulation trap. The contents of the backup trap was then analysed at intervals by GC–flame ionisation detection (FID), to construct the frontal analysis S-curve. During the GC analysis of the second trap, the flow of standard through the first trap was stopped. Before analysis of the backup trap by GC, the trap is centrifuged for 2 min to remove any excess water and thus avoid the introduction of water into the GC. After centrifugation, the MC8 trap is placed into the programmed-temperature vaporizer (PTV) inlet in the inverted position for reverse flow desorption. The inlet has a starting temperature of 30°C, and is heated to 250°C within about 2 min. The temperature of the column is maintained at 30°C for 10 min. The column is then programmed at 10°C/min to 250°C. The linear flow-rate of the hydrogen carrier gas is 50 cm/s.

3.2. Analytical instrumentation

With the breakthrough volume tests of single components a Waters Associates absorbance detector, Model 441 was used. GC–FID analysis of the multichannel silicone-rubber traps were performed on a Varian Series 3700 GC system fitted with a PTV injector [21] for thermal desorption of the MC8 trap and a Chrompack desorber for the thermal desorption of the MC32 trap. The GC system is fitted with a glass capillary column (25 m×0.3 mm), coated with a 0.4 μm layer of polydimethylsilicone.

4. Results and discussion

4.1. Determining number of plates and breakthrough volume for MC8 traps

Tables 3 and 4 indicate the results obtained in the study to determine which experimental method (equation) produces the most reliable number of plates and breakthrough volumes for the MC8 trap. Initial tests were performed with phenol which is polar and thus hardly retained in the non-polar silicone phase of the multichannel trap. Due to the bad retention of phenol in the silicone phase, non-symmetric elution and frontal curves were obtained (see Fig. 2) and thus it was difficult to obtain accurate parameters to determine the number of plates of the trap and the breakthrough volume for phenol. This is also the reason for the bad relative standard deviations (RSDs) obtained for phenol. With benzene, which is non-polar and better retained on the silicone stationary phase better elution and frontal curves (see Fig. 3) were obtained, leading to more reproducible results.

From the elution analysis results obtained for benzene in Table 3, Eqs. (2), (4) and (8) gave similar results. The statistical moments of the elution peaks were calculated according to the HP Chemstation manual [22] and then applied to Eq. (8). For benzene, the values of N obtained with Eq. (8) did not significantly vary from those obtained with Eqs. (2) and (4). The experiments with phenol gave a large variation in results, due to the more asymmetrical peaks obtained for phenol.

With the frontal analysis experiments, the results using Eq. (11) correlate the best with those obtained from the elution analysis experiments and have the smallest RSD value. For further frontal analysis experiments Eq. (11) is thus used to determine the number of plates (N) and for elution analysis Eq. (4) is used. For practical reasons, Eq. (4) is easier to use than Eq. (8). Due to the non-symmetrical peaks obtained with traps, Eq. (4) is preferred over Eq. (2) as it uses the more informative width at the base of the peak compared to the width at 0.882 of the maximum peak height (σ) [23]. The effect of dead volumes in the detector and connection lines on the number of plates was calculated and found to be negligible. No significant deviations were found

Table 3
Comparing different methods of experimentally determining the number of plates of the MC8 trap for phenol and benzene at 75 μl/min

Exp. No.	*N* for phenol							
	Elution analysis				Exp. No.	Frontal analysis		
	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (8)		Eq. (9)	Eq. (10)	Eq. (11)
1	10	8.0	9.4	5.4	7	10	3.7	4.0
2	5.0	3.5	5.5	2.6	8	14	16	5.6
3	3.6	3.6	2.4	2.5	9	14	8.2	5.6
4	2.2	1.0	2.8	1.3	10	24	11	9.5
5	3.5	2.6	8.9	2.6	11	13	3.8	5.1
6	4.7	3.4	9.4	4.4	12	17	6.4	6.6
Average	4.9	3.7	6.4	3.1		15	8.1	6.1
RSD (%)	52	58	47	47		28	52	28
	N for benzene							
13	4.3	1.9	4.6	5.1	19	13	3.2	5.1
14	3.5	1.4	3.3	4.0	20	13	3.5	4.9
15	5.7	2.7	5.8	6.3	21	11	3.5	4.4
16	3.8	1.4	4.0	5.2	22	9.1	2.0	3.6
17	2.9	0.8	3.3	3.9	23	11	3.3	4.4
18	3.4	1.4	3.6	4.2				
Average	3.9	1.6	4.1	4.7		11	3.1	4.5
RSD (%)	23	35	22	19		12	19	12

Table 4
Comparing different methods of experimentally determining the breakthrough volume of phenol and benzene at 75 μl/min with the MC8 trap

Exp. No.	V_b in ml for phenol					
	Elution analysis			Exp. No.	Frontal analysis	
	Eq. (18)	Eq. (12)[a]	Eq. (13)[a], loss 5%		Eq. (12)[b]	Eq. (13)[b], loss 5%
1	0.09	0.07	0.09	7	0.00	0.10
2	0.06	0.03	0.09	8	0.02	0.10
3	0.02	−0.05	0.07	9	0.02	0.09
4	−0.01	−0.01	0.03	10	0.09	0.20
5	0.01	0.02	0.03	11	0.03	0.19
6	0.02	0.03	0.04	12	0.06	0.21
Average	0.03	0.02	0.06		0.04	0.15
RSD (%)	102	246	45		78	36
	V_b in ml for benzene					
13	3.0	1.0	9.9	19	1.3	7.5
14	1.8	−1.5	8.4	20	1.1	7.8
15	4.9	2.7	11	21	0.5	6.4
16	1.8	−0.1	7.1	22	−0.6	6.7
17	0.4	−1.2	6.6	23	0.5	6.2
18	1.1	−0.4	5.8			
Average	2.2	0.05	8.1		0.5	6.9
RSD (%)	67	2892	23		127	9

[a] The number of plates were calculated by using Eq. (4).
[b] The number of plates were calculated by using Eq. (11).

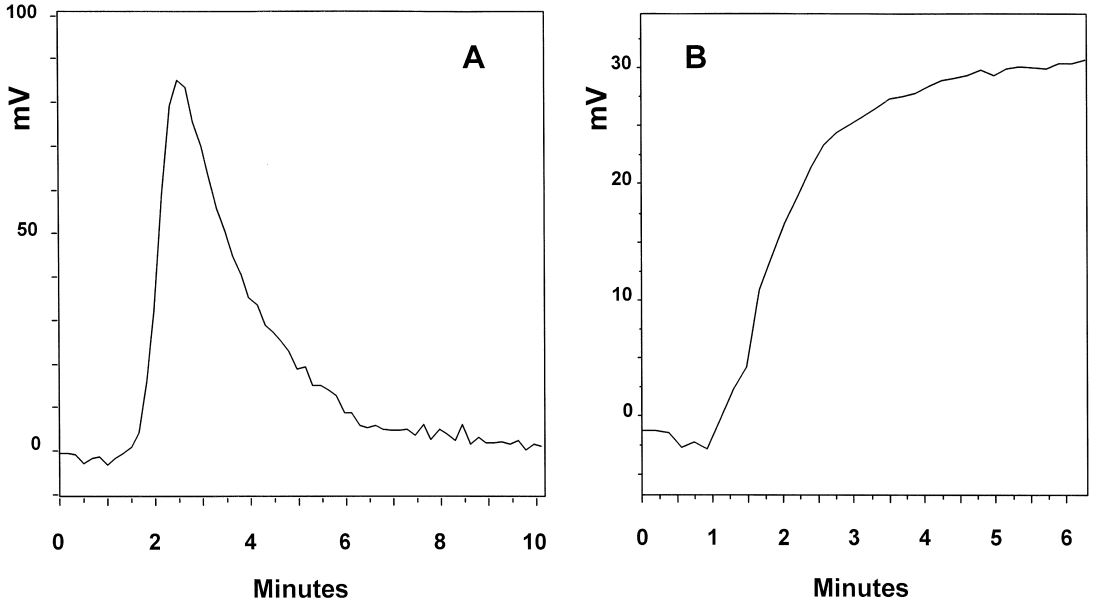

Fig. 2. (A) Elution and (B) frontal breakthrough curves of phenol through the MC8 trap at 75 μl/min.

when the collection efficiencies of different MC8 traps were compared.

Table 4 indicates the results obtained for the determination of the breakthrough volume of phenol and benzene at 5% ''loss'' with the different methods available. The results with Eq. (12) do not correlate with those obtained with Eqs. (18) and (13). Eq. (12) is also only valid for traps with $N>4$; at lower plate numbers, a negative value is obtained for V_b. Using Eq. (13) to calculate the V_b, larger volumes are obtained than when Eq. (18) is used. With the use of Eq. (18) it is assumed that symmetrical Gaussian peaks are obtained and that N is greater than 9. As $N=4$ for the MC8 trap at a flow-rate of 75 μl/min, the elution peaks obtained are not totally symmetrical and thus the equations in Table 2 cannot be

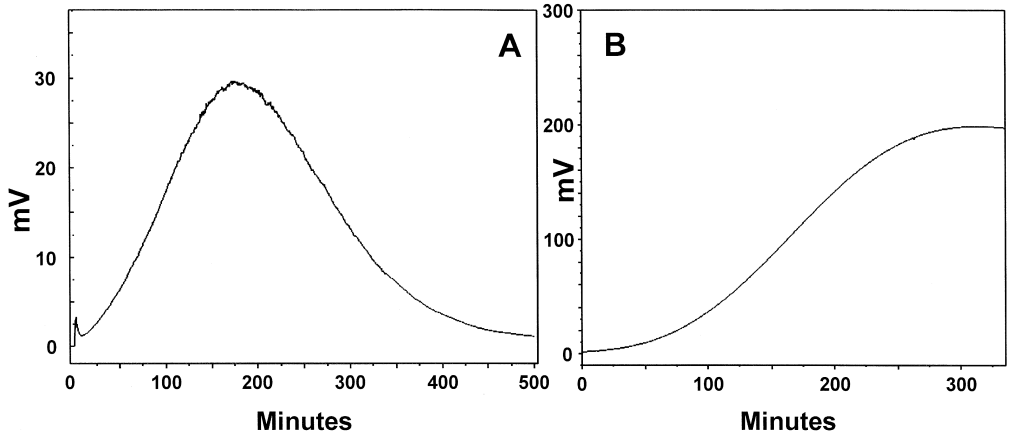

Fig. 3. (A) Elution and (B) frontal breakthrough curves of benzene through the MC8 trap at 75 μl/min.

applied for the calculation of V_b. It was shown by Lövkvist and Jönsson [18] that Eq. (13) could be used for very low plate numbers, i.e., $N=0.2$. Also the V_b of 0.15 ml obtained for phenol using Eq. (13) correlates better with the calculated void volume, 0.11 ml, of the MC8 trap, indicating slight retention of phenol on the silicone trap.

From Tables 3 and 4 we see that the number of theoretical plates, *N*, for the MC8 trap is 4 and the breakthrough volumes of phenol and benzene are 0.15 ml and 6.9 ml, respectively, at a flow-rate of 75 μl/min. Due to the nature of phenol, its retention in the silicone-rubber tubing of the trap could be improved by decreasing the pH of the sample. More research still needs to be done in this direction.

A further study was aimed at obtaining *N* and V_b at 75 μl/min for the less volatile compounds naphthalene, acenaphthene, fluorene, pyrene and chrysene, using the frontal analysis technique. In this case the data was obtained by the GC method of analysis of the backup trap. The naphthalene results were non-conclusive due to the loss of naphthalene from the water standard into the atmosphere during sampling. Acenaphthene and fluorene gave good S-curves (see Fig. 4). The curves for the more retained pyrene and chrysene were very flat and did not reach total breakthrough even at 3500 ml elution volume when the experiment was ended.

From the S-curves for acenaphthene and fluorene, breakthrough volumes of 632 ml and 732 ml, respectively were obtained at a flow-rate of 75 μl/min. The corresponding plate numbers were 3.7 and 4.1 for these two compounds.

Some literature is available for indirect comparison with our results: Burger and Le Roux [5] collected dichloromethane from water with a 1 m single channel OTT which has a similar total length of silicone tubing as our MC8 trap at a flow-rate of 16 μl/min. At this flow-rate dichloromethane had a breakthrough volume of ca. 2 ml. Mol et al. [19] found that trapping naphthalene from a methanol–water (26:74, v/v) sample with a 2 m OTT, breakthrough occurred at 800 μl when sampling at a flow-rate of 45 μl/min.

The capacity factors, *k*, for phenol, benzene, acenaphthene and fluorene for the MC8 trap at 25°C are 1.7, 98, 9332 and 10 395, respectively, as determined from V_R for each compound and the calculated hold up volume of the trap, according to Eq. (1). The phenol and benzene capacity factors for the MC8 trap compare well with the values 2.6 and 140, calculated from poly(dimethylsiloxane)–water

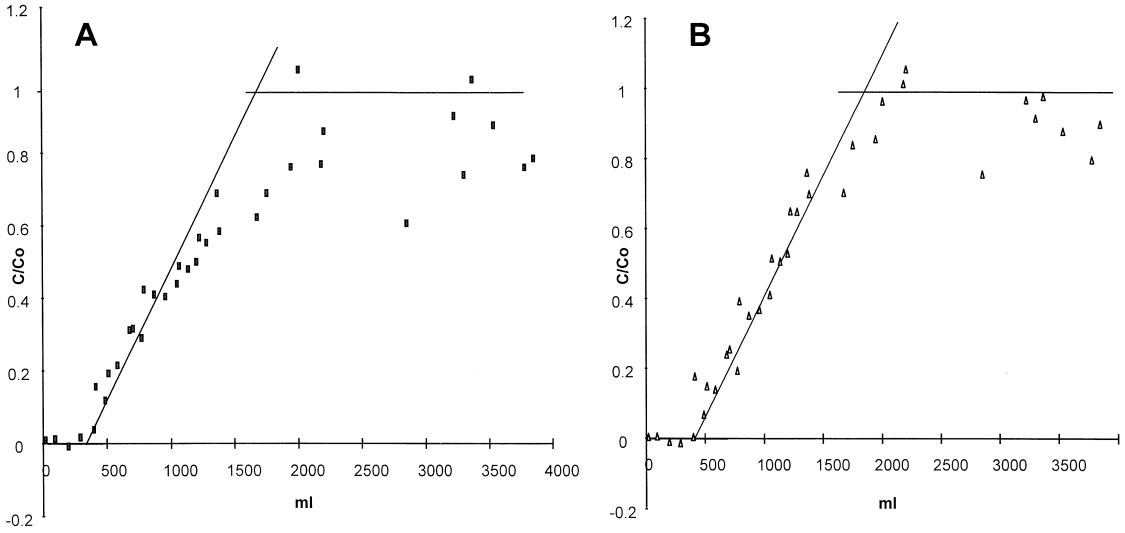

Fig. 4. Frontal breakthrough data points of (A) acenaphthene and (B) fluorene. Trapping was performed at 75 μl/min with a second MC8 trap coupled to the exit of the first trap. Breakthrough data points were obtained by analysing the contents of the second MC8 trap by GC–FID.

Table 5
The effect of flow-rate on N and V_b, using the elution analysis technique with Eqs. (4) and (13), respectively

Flow-rate (μl/min)	Phenol			Benzene		
	V_R (ml)	N	V_b (ml)	V_R (ml)	N	V_b (ml)
75	0.09	6.4	0.06	12	4.1	8.1
50	0.21	5.5	0.17	12	5.1	8.2
20	0.30	9.0	0.20	12	8.7	9.5

distribution constants (K) obtained with a 100 μm SPME fibre [24,25] and the phase ratio (β) of our MC8 trap.

4.2. The effect of flow-rate on MC8 efficiency

Table 5 shows how the number of plates, N, for the MC8 trap and thus also the breakthrough volumes for phenol and benzene increase with decreasing flow-rate. This correlates with the Van Deemter theory [26] of chromatographic movement of compounds through a column, i.e., decreasing theoretical plate height with decreasing linear flow-rate. As expected the retention volume for both compounds are unaffected by the flow-rate.

At a flow-rate of 20 μl/min a plate number of 9 is obtained, correlating well with results obtained by Mol et al. [19] of 10 plates per metre with their 2 m single channel trap at a flow-rate of 25 μl/min. The total length of silicone tubing in our MC8 trap is approximately 85 cm.

4.3. The effect of concentration on collection efficiency

Table 6 indicates no significant variation in retention volume and breakthrough volume with increasing concentration of benzene. There appears to be a variation in the number of plates but this is only slight and probably due to the technique used to calculate N. This indicates that the extraction efficiency of the trap does not change, even at concentrations of 218 μg/ml and possibly higher.

Table 7
Comparison between multichannel traps[a]

	MC1[b]	MC8	MC32
No. tubes parallel	1	8	32
Length silicone (m)	1	0.84	2.56
V_0 (μl)	45	111	379
V_s (μl)	175	220	752
β	0.26	0.5	0.5
F_v (μl/min)	75	75	75
F_l (mm/min)	1658	71	18
N		4	11
V_b (ml) (benzene)		8	37
V_R (ml) (benzene)		11	44
Exp. k (benzene)		98	115

[a] N and V_b for both traps were calculated using the elution analysis technique with Eqs. (4) and (13), respectively.
[b] Taken from Ref. [5].

4.4. The effect of trap configuration on collection efficiency

A Chrompack thermal desorber with cryogenic focusing facilities was recently acquired to improve the analysis of more volatile compounds from the multichannel trap. This desorber takes traps that have an O.D. of 6 mm. New traps were thus made in glass tubing (160×0.4 mm I.D.) by placing 32 (90 mm) silicone-rubber tubes in parallel inside the trap (MC32). For comparison with the MC8 trap, the number of plates and breakthrough volume of benzene was determined for the MC32 trap. Table 7

Table 6
The effect of concentration on N and V_b using a benzene aqueous standard and working at a flow-rate of 75 μl/min[a]

Concentration (μg/ml)	Benzene ($n=3$)		
	V_R (ml) (RSD, %)	N (RSD, %)	V_b (ml) (RSD, %)
9	12 (3.4)	4.5 (22)	8.0 (11)
87	12 (1.8)	6.4 (9.9)	8.8 (1.3)
178	11 (6.3)	4.8 (6.3)	7.2 (8.2)
218	11 (2.0)	7.4 (6.5)	8.8 (3.7)

[a] The frontal analysis technique was used with Eqs. (11) and (13), respectively.

shows a comparison between properties of the multichannel traps and a single channel trap of Burger and Le Roux [5].

From Table 7 it can be seen that the length of silicone tubing and the volume of stationary phase (V_s) for the MC8 trap and the single channel trap is very similar. The volume of the mobile phase (V_0) and therefore also the phase ratio (β), of the MC8 is about double that of the single channel trap. The volume of the mobile phase is much greater than that of the single channel trap due to the open spaces between the silicone tubes. In Table 7 it is noted that at a volume flow-rate of 75 μl/min, the linear flow-rate decreases from 1658 mm/min to 18 mm/min, for a single channel trap to a multichannel 32 trap. The decrease in linear flow, as expected, causes the N to increase from 4 for the MC8 trap to 11 for the MC32 at a volume flow-rate of 75 μl/min. Thus the V_b for benzene increased from 8 ml to 37 ml (more than a factor 4) at the same volume flow-rate of 75 μl/min when changing the configuration of the trap from MC8 to MC32.

5. Conclusion

Different techniques were evaluated for the experimental determination of the theoretical number of plates of a sorption trap and the associated breakthrough volumes of a number of compounds. Reliable equations were identified that gave consistent values of N with different sample analysis methods, i.e., online by UV and offline with GC–FID, for compounds with widely varying k values.

The number of plates at various flow-rates were determined for the MC8 trap, the highest value, $N=9$ being obtained at the lowest flow-rate of 20 μl/min. By changing the configuration of the multichannel trap to 32 silicone tubes in parallel, a plate number of 11 could be obtained with a much higher volume flow-rate of 75 μl/min. The increased efficiency of the MC32 trap allows higher sampling flow-rates resulting in decreased sampling times.

The high breakthrough volumes obtained, 37 ml to 732 ml for benzene and fluorene, respectively, allows for quantitatively analysis of samples in the ppb and ppt levels. The extraction efficiency of the trap does not vary over a large concentration range (up to 218 μg/ml) as expected for the retention mechanism of absorption into a thick film of stationary phase.

The desorption of compounds from the MC32 trap with a commercially available thermal desorber with cryogenic focusing facilities, allows for the analysis of more volatile compounds. With increased breakthrough volumes obtained for the MC32 trap, a wide boiling point range of compounds can quantitatively be analysed. The open structure of the multichannel trap allows sampling with gravity flow, simplifying laboratory procedure and instrumentation. These qualities pave the way for the routine use of multichannel traps in trace organic analysis of aqueous samples.

References

[1] C.L. Arthur, D.W. Potter, K.D. Buchholz, S. Motlagh, J. Pawliszyn, LC·GC 10 (1992) 656–661.
[2] S. Blomberg, J. Roeraade, J. High Resolut. Chromatogr. 13 (1990) 509–512.
[3] H.G.J. Mol, H.G. Janssen, C.A. Cramers, J. High Resolut. Chromatogr. 16 (1993) 413–418.
[4] G. Goretti, M.V. Russo, E. Veschetti, Chromatographia 35 (1993) 653–660.
[5] B.V. Burger, M. Le Roux, J. Chromatogr. 642 (1993) 117–122.
[6] H.G.J. Mol, H.G. Janssen, C.A. Cramers, U.A.Th. Brinkman, J. Microcol. Sep. 7 (1995) 247–257.
[7] E. Baltussen, H.G. Janssen, P. Sandra, C.A. Cramers, J. High Resolut. Chromatogr. 20 (1997) 385–393.
[8] E. Baltussen, H.G. Janssen, P. Sandra, C.A. Cramers, J. High Resolut. Chromatogr. 20 (1997) 395–399.
[9] E. Baltussen, F. David, P. Sandra, H.G. Janssen, C. Cramers, J. High Resolut. Chromatogr. 21 (1998) 645–648.
[10] E.K. Ortner, E.R. Rohwer, J. High Resolut. Chromatogr., in press.
[11] A. Raymond, G. Guiochon, J. Chromatogr. Sci. 13 (1975) 173–177.
[12] J.J. Kirkland, W.W. Yau, H.J. Stoklosa, C.H. Dilks Jr., J. Chromatogr. Sci. 15 (1977) 303–316.
[13] W.W. Yau, Anal. Chem. 49 (1977) 395–398.
[14] J.P. Foley, J.G. Dorsey, Anal. Chem. 55 (1983) 730–737.
[15] A.S. Said, H. Al-Ali, E. Hamad, J. High Resolut. Chromatogr. 5 (1982) 306–310.
[16] H. Purnell, Gas Chromatography, Wiley, New York, 1962.
[17] C.N. Reilley, G.P. Hilderbrand, J.W. Ashley, Anal. Chem. 34 (1962) 1198–1213.
[18] P. Lövkvist, J.Å. Jönsson, Anal. Chem. 59 (1987) 818–821.
[19] H.G.J. Mol, J. Staniewski, H.G. Janssen, C.A. Cramers, R.T. Ghijsen, U.A.Th. Brinkman, J. Chromatogr. 630 (1993) 201–212.

[20] E.K. Ortner, E.R. Rohwer, J. High Resolut. Chromatogr. 19 (1996) 339–344.
[21] P.J. Apps, V. Pretorius, K.H. Lawson, E.R. Rohwer, M.R. Centner, H.W. Viljoen, G. Hulse, J. High Resolut. Chromatogr. 10 (1987) 122–127.
[22] Understanding Your Chemstation, Hewlett-Packard, 1994.
[23] A.S. Said, Theory and Mathematics of Chromatography, Hüthig, Heidelberg, 1981.
[24] K.D. Buchholz, J. Pawliszyn, Anal. Chem. 66 (1994) 160–167.
[25] J.J. Langenfeld, S.B. Hawthorne, D.J. Miller, Anal. Chem. 68 (1996) 144–155.
[26] P. Sandra, J. High Resolut. Chromatogr. 12 (1989) 273–277.