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Journal of Chromatography A, 791 (1997) 177–185

JOURNAL OF CHROMATOGRAPHY A

Novel preconcentration technique for on-line coupling to high-speed narrow-bore capillary gas chromatography: sample enrichment by equilibrium (ab)sorption
I. Principles and theoretical aspects

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Received 8 April 1997; received in revised form 8 July 1997; accepted 8 July 1997

Abstract

In recent years, there has been substantial progress in the field of high-speed narrow-bore capillary gas chromatography (GC) in general, and in the development of (trans)portable gas chromatographs for fast and accurate analysis in field applications in particular. Due to the limited (concentration) sensitivity of instrumentation for high-speed (portable) GC, environmental applications of this technique frequently require a preconcentration step. The equilibrium (ab)sorption technique described in this article was found to be very promising for on-line coupling to high-speed narrow-bore capillary GC and field portable GC instruments. Enrichment factors up to at least 100 can be obtained rapidly without the use of complicated instrumentation. The new preconcentration technique is shown to have clear advantages over enrichment based on conventional adsorption, i.e. thermal desorption techniques. It can be carried out at ambient trapping temperatures, gives uniform desorption profiles, reduces water effects, uses inert adsorption materials and does not require a (cryogenic) refocusing step. Moreover, the new preconcentration method allows the enrichment factors to be predicted from tabulated chromatographic data, thereby facilitating calibration. © 1997 Elsevier Science B.V.

Keywords: Trace analysis; Sample enrichment; Equilibrium absorption; Preconcentration

1. Introduction

Despite the tremendous progress in detection techniques for gas chromatography (GC), the analysis of low concentrations of target solutes in gaseous samples still often requires enrichment of the sample prior to its introduction into the gas chromatograph. Most of the sample enrichment techniques for gaseous samples currently in use in GC are based on the principle of adsorption–thermal desorption (ATD) using solid adsorption materials [1–4].

On-line coupling of an ATD-based enrichment device with high-speed narrow-bore capillary GC is complicated, due to the very strict requirement for a narrow input band-width. One way to meet this demand is to incorporate a cryofocusing step to refocus the solutes on the analytical column. Van Es et al. [5] developed a microcryofocusing device that is capable of generating the very narrow input band-widths required for high speed narrow-bore capillary GC. The device was later improved by Borgerding

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0021-9673/97/$17.00
PII S0021-9673(97)00771-1

and Wilkerson [6]. With such a system, ATD-based techniques are, at least in principle, also suited for combination with narrow-bore capillary GC. If, for example, for reasons of portability, the use of cryogenic refocusing is not possible, packed micro-traps, such as those reported by Frank and Frank [7] and Mitra et al. [8–11], have to be used for on-line enrichment with narrow-bore fast GC analysis. Despite the extremely low volume of these traps, the band-width requirements of narrow-bore capillary GC are still not fully satisfied. A sufficiently fast transfer of the desorbed solutes onto the chromatographic system can only be obtained for a mega-bore, e.g. 530 μm I.D. analytical column, which allows a high gas flow-rate during the desorption step.

An important and growing application area of high-speed narrow-bore capillary GC is the area of field-(trans)portable analytical devices. Unfortunately, these instruments have a limited applicability in environmental analysis, as their detection limits are generally in the low parts per million range [12]. For the analysis of components present at lower concentrations, the field-portable GC has to be equipped with a suitable preconcentration device. As explained above, the direct on-line coupling of ATD-based techniques to field portable GC instruments equipped with a narrow-bore GC column is difficult at best [13]. This is not only because cryogenics cannot be used in portable instruments but also because these instruments often use silicon-micromachined injection valves that operate according to the ''time-slice'' injection principle. Until now, only an off-line enrichment technique compatible with portable high-speed GC was reported [14].

In this work, we have developed a new sample preconcentration/enrichment technique, the technique of equilibrium (ab)sorption. With this new sample-enrichment technique, the standard silicon-micromachined injection valves used as injectors in portable GC instruments can be used without modification. The new technique is capable of the on-line generation of an homogeneously enriched sample flow. Any part of this flow is representative for the entire sample and, therefore, it enables reproducible injection into the GC system. The need to transfer the entire desorption volume onto the analytical column is thus eliminated. The volume to be injected now can be adjusted to the requirements of the chromatographic system and the use of a refocusing step is no longer necessary. This feature is clearly very advantageous for high-speed narrow-bore capillary GC, in which the injection volume is a critical parameter. The latter injection method is used not only for portable micro gas chromatographs, but has been proven to be the best injection technique for high speed narrow-bore capillary GC in general (A. Van Es, thesis). In this paper, the principles and theoretical aspects of the new method are discussed. In further contributions, following this paper, analysis of selected hydrocarbons and volatile organic compounds (VOCs) in air, using an on-line system consisting of a preconcentration device based on equilibrium (ab)sorption and a field-portable GC, will be reported.

2. Theory

In previous work, silicon-micromachined injection valves have been found to be excellent systems for the introduction of (gaseous) samples in high-speed narrow-bore capillary GC [15]. The injection valves operate according to the principle of ''time-slicing''. Fig. 1 shows a schematic diagram of a silicon-micromachined injection valve as used in the field-portable GC. The gas sample is pressurized inside the sample loop. The silicon-micromachined injection valve is then opened for a fraction of a second to allow a part of the contents of the sample loop to enter the chromatographic column. Short injection

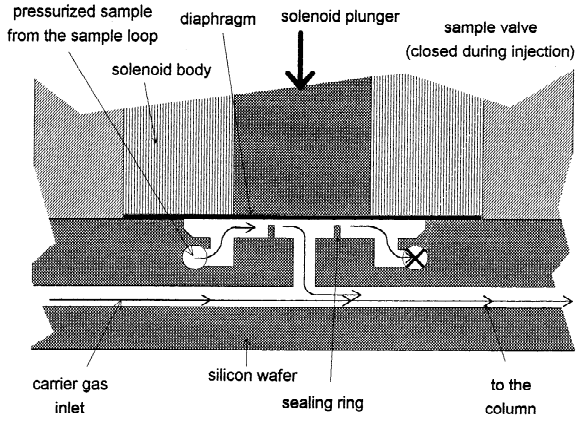

Fig. 1. Cross-sectional diagram of the silicon-micromachined injection valve. The valve is in the open (inject) position.

times, typically in the range of 10 to 250 ms, result in a very narrow input band-width. This injection technique is not compatible with ATD techniques, as unpredictable desorption profiles are obtained with these methods. If the ''injection slice'' is taken from the first part of the desorption volume, only the volatile solutes are recovered and vice versa. Time-slicing injection techniques are only compatible with ATD if the trap is strictly miniaturized so that the entire volume of the desorption gas can be transferred onto the GC column. When using narrow-bore columns (I.D.$<$100 μm), this is virtually impossible.

To overcome this disadvantage, we developed a preconcentration method that produces a steady flow of homogeneous, preconcentrated sample gas, i.e., the method of equilibrium (ab)sorption. An additional advantage of this technique is that the enrichment factors do not have to be established experimentally as they can be calculated from GC retention data. The theoretical background of this method is described below.

2.1. Equilibrium (ab)sorption procedure

In the equilibrium (ab)sorption technique, a steady flow of enriched sample gas is generated. To do so, a large volume of the gas sample that is to be enriched is pumped through a tube packed with an (ab)sorption material at a mild, e.g. ambient, temperature. Sampling is continued until the (ab)sorption material in the trap is saturated with the components of interest. More precisely, sampling is continued until the sorbent phase is in equilibrium with the gas phase. Once this equilibrium has been achieved, the trap is closed and the system is heated to shift the equilibrium from the sorbed state to the gas phase. Unlike the situation in the ATD method, sampling is continued beyond the breakthrough point. To avoid oxidation of the sorbent phase at high temperatures, the air is eliminated from the trap by briefly purging it with helium prior to starting the heating step. Heating is performed under stopped-flow conditions to a predetermined (high) temperature.

2.2. Prediction of the enrichment factor

In order to allow the rapid equilibration of the entire bed of (ab)sorption material in a reasonably short time while simultaneously allowing the quantitative desorption of the trapped components at a mild temperature, the use of a weak (ab)sorption material is advisable. This is in contrast to the conventional breakthrough sampling approach, where it is better to use a strong adsorbent. Moreover, to produce a stable desorption profile, the sorbent bed has to be homogeneous and the concentration of the solutes has to be fairly stable within the sampling time. Other disadvantages arising from the use of solid adsorbents include the competitive nature of the adsorption process, the large water vapor effect and the influence of the residue active sites on the adsorbent surface. In this work, we opted for the use of a mega-bore thick-film non-polar wall-coated open tubular (WCOT) column as the preconcentration trap. Sorption of the components is now based on a pure partitioning mechanism, which is relatively weak. This allows the rapid equilibration of the sorption tube. In addition to this, the use of an open tubular preconcentration device gives the required homogeneity to the desorption plug. Finally, because adsorption is solely based on partitioning, the enrichment factor can be readily calculated from GC retention data. The enrichment factor that can be achieved by the procedure, $E_{T_1-T_2}$, can be defined as:

$$E_{T_1-T_2} = \frac{c_{\mathrm{m},T_2}}{c_{\mathrm{m},T_1}} \tag{1}$$

where c_{m,T_1} is the concentration of the component of interest in the original flow of sample gas at temperature T_1 and c_{m,T_2} is its concentration in the enriched sample gas stream coming from the tube at temperature T_2. Using standard chromatographic theory, these parameters can be expressed as:

$$c_{\mathrm{m},T_2} = \frac{c_{\mathrm{s},T_2}}{K_{\mathrm{D},T_2}} = \frac{c_{\mathrm{s},T_2}}{k_{T_2}\beta} \tag{2}$$

$$c_{\mathrm{m},T_1} = \frac{c_{\mathrm{s},T_1}}{K_{\mathrm{D},T_1}} = \frac{c_{\mathrm{s},T_1}}{k_{T_1}\beta} \tag{3}$$

where c_{s,T_1} and c_{s,T_2} are the concentrations of the component of interest in the stationary phase; k_{T_1} and k_{T_2} are the respective capacity factors and K_{D,T_1} and K_{D,T_2} are the partitioning coefficients at temperatures T_1 and T_2, respectively. β is the phase ratio of the trapping column.

The total amount of a solute in the trap after sampling, m_{trap}, is given by:

$$m_{trap} = c_{m,T_1} \cdot V_m + c_{s,T_1} \cdot V_s \quad (4)$$

where V_m and V_s are the mobile phase and the stationary phase volumes of the column, respectively. During the helium purging step that is applied to remove air, an amount roughly equal to the first term on the right hand side of Eq. (4) is lost. After heating the trap, the total amount can again be expressed by an equation similar to Eq. (4), but now with the T_2 indexes. This results in:

$$c_{s,T_1} \cdot V_s = c_{s,T_2} \cdot V_s + c_{m,T_2} \cdot V_m \quad (5)$$

After substitution of Eq. (2) into this equation, we have the following relationships:

$$c_{s,T_1} = (k_{T_2} + 1) \cdot c_{m,T_2} \cdot V_m \quad (6)$$

or

$$c_{m,T_2} = \frac{c_{s,T_1} \cdot V_s}{V_m \cdot (k_{T_2} + 1)} = \frac{c_{s,T_1}}{\beta \cdot (k_{T_2} + 1)} \quad (7)$$

Combining Eqs. (1), (3), (7) gives the final relationship for the enrichment factor:

$$E_{T_1-T_2} = \frac{k_{T_1}}{k_{T_2} + 1} \quad (8)$$

As can be seen from this equation, the enrichment factor is roughly equal to the capacity factor of the solute at the sorption temperature used in the sampling process. This is because at the high temperature used for desorption, the solute's capacity factor is usually much smaller than one. Eq, 8 also shows that the enrichment factor can be easily obtained experimentally by simply measuring the capacity factors of the solute at two temperatures on a column coated with the same stationary phase, but not necessarily with the same film thickness.

Alternatively, the capacity factors of the solutes at the two temperatures employed in the preconcentration procedure can be extracted from the Kovat's retention indices using the procedure mentioned in Ref. [16]:

$$\ln k = \ln \frac{\alpha}{\beta} + \frac{\Delta H}{RT} \quad (9)$$

where (α/β) is the so-called entropy term and $(\Delta H/R)$ is the enthalpy term.

Using the same considerations, we can calculate the minimum time required for sampling, i.e., the time required to reach the equilibrium state at a temperature, T_1. This time equals the elution time of the components using air as the carrier gas. If we neglect the pressure drop across the trapping column and if we further assume that the column has an infinitely large number of theoretical plates, the required minimum sampling time is given by:

$$t_{sampl.} = t_M \cdot (k_{T_1} + 1) = \frac{V_m}{v_{T_1}} \cdot (k_{T_1} + 1) \quad (10)$$

where v_{T1} is the sampling flow-rate measured at the outlet of the trapping column.

2.3. Effect of a pressure drop

In Section 2.2, it was assumed that no pressure gradient exists over the trap, either during sampling or desorption. It will be demonstrated below that the compressibility of the gas streams can have a significant influence on the composition of the enriched sample.

The variation of the gas pressure $p(x)$ along a capillary column of length, L, is described by the following equation:

$$p(x) = p_o \cdot \sqrt{\left(\frac{p_i}{p_o}\right)^2 - \frac{x}{L}\left[\left(\frac{p_i}{p_o}\right)^2 - 1\right]} \quad (11)$$

where x is the distance from the column inlet. The terms p_i and p_o represent the column inlet and outlet pressures, respectively. This relationship is graphically shown in Fig. 2. The existence of a pressure gradient across the column has significant consequences for the local concentrations of the solute molecules. The concentration of the solute in the mobile phase, expressed as mass per unit volume, follows the pressure pattern along the trapping column. This now means that the solute concentration (expressed as mass per unit volume) in the stationary phase in equilibrium with the mobile phase also decreases from a higher value at the inlet

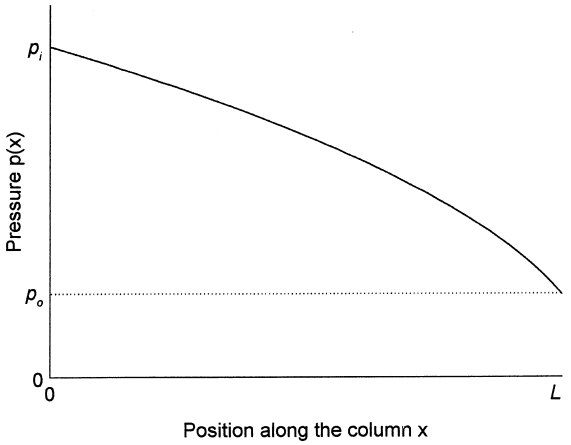

Fig. 2. Pressure gradient along the open tubular capillary column.

to a lower value at the outlet. A concentration gradient occurs in the stationary phase, reflecting the pressure drop in the mobile phase.

To fulfil the requirement of a stable desorption profile, the concentration difference between the starting point and the end point of the concentration gradient should not be higher than (arbitrarily) 10%. This results in the requirement that the pressure drop over the trapping column during sampling is less than 10%, i.e. $(\Delta p/p_i.) \leq 0.1$. In practice, in order to avoid possible contamination of the trap, the gas sample stream is pulled through the adsorption tube by means of a vacuum pump rather than being pumped through the trap at elevated pressures. This means that the inlet pressure, p_i, will be maintained at ambient pressure (1 bar). The outlet pressure, p_o, then should not be lower than 0.9 bar.

2.4. Sampling flow-rate

For practical reasons, the sampling time should be as short as possible. This means that the use of higher sampling flow-rates for equilibration of the trap is desirable. However, this should not result in pressure drops exceeding 10% of the inlet pressure. In the case of open tubular columns, the volumetric flow-rate through the column at a given inlet and outlet pressure can be calculated according to the Hagen–Poiseuille equation [17]. The results of the calculation for different column sizes at various pressure drops are shown in Table 1. For air samples, the viscosity at 30°C is approximately 200 $\mu P = 2 \cdot 10^{-4}$ g/cm.s [17]. For a number of columns, experimental values were also measured. Lower measured values for the larger-bore columns compared to

Table 1
Inlet flow of gas through open-tubular trapping columns of different dimensions and at different pressure drops

p_i (bar)	p_o (bar)	d_c (μ)	L (m)	V_c (ml)	F (ml/min)	
					Calculated	Measured
1	0.9	530	20	4.412	2.9	3.0
1	0.5	530	20	4.412	11.5	13.5
1	0.3	530	20	4.412	13.9	17.5
1	0.9	530	10	2.206	5.8	6.5
1	0.5	530	10	2.206	22.9	21.5
1	0.3	530	10	2.206	27.8	26.8
1	0.9	530	5	1.103	11.6	7.8
1	0.5	530	5	1.103	45.9	25.6
1	0.3	530	5	1.103	55.7	
1	0.9	750	5	2.209	46.6	
1	0.5	750	2	0.884	116.5	
1	0.3	750	1	0.442	233.0	
1	0.9	1000	5	3.927	147.3	
1	0.9	1000	2	1.571	368.2	
1	0.9	1000	1	0.785	736.3	200.0
1	0.9	2000	5	15.708	2356.2	
1	0.9	2000	2	6.283	5890.5	
1	0.9	2000	1	3.142	11781.0	

the calculated data are most likely due to extra restriction effects in the valves and tubing used in the experimental set-up.

2.5. Requirements for the open tubular trapping column

From the theoretical considerations described above, several requirements that the trapping column has to meet can be identified. First of all, the trapping column should generate a sufficiently large volume of enriched sample to flush the transfer lines to the GC injector. Furthermore, a certain minimum plate number is required to obtain a stable concentration profile. Moreover, there is a maximum allowable pressure drop. These parameters are examined below in more detail.

The volume of enriched sample that is generated by the trapping column during desorption has to be large enough to thoroughly flush the connecting lines and sample loop of the GC instrument. The sampling and injection system of a portable GC instrument typically has an internal volume of 200 to 500 μl. The trapping column therefore should have a volume V_c of approximately 2 ml or more, sufficient to flush the inlet system four to ten times. This criterium is met for all columns described by the following equation:

$$L \geq \frac{4 \cdot V_c}{\pi \cdot d_c^2} = \frac{2.548 \cdot 10^{-6}}{d_c^2} \qquad (12)$$

Eq. (10) indicates that the minimum sample volume that has to be passed through the trapping column to reach equilibrium is at least $(k_{T_1} + 1)$ times larger than the volume of the column itself. This relationship is valid only if the trapping column has an infinite plate number. In practice, a correction factor must be incorporated into the equation to correct for the finite plate number of the trap. The sample volume needed for 95% breakthrough [18] is:

$$V_{\text{sampl.}} = V_c \cdot (k_{T_1} + 1) \cdot \left(1 + \frac{2.326}{\sqrt{N}}\right) \qquad (13)$$

where N is the plate number of the column. If the trapping column has a volume of 2 ml, 100 theoretical plates and if the capacity factor of the component at the low sampling temperature is 100 (enrichment factor is approx. 100), the sample volume needed for 95% breakthrough is approximately 125 ml. To ensure full equilibration, the sample volume should be even larger. In order to complete the sample pretreatment procedure in a reasonably short time, the sampling flow-rate, F, should be sufficiently high. In our consideration, a sampling flow-rate of some 100 ml/min would be appropriate. This, however, should not result in an excessive pressure drop. The column dimensions that can give a flow-rate of 100 ml/min at an inlet pressure of 1 bar and an outlet pressure of 0.9 bar are given by:

$$L = \frac{\pi \cdot d_c^4}{128 \cdot \eta \cdot F} \cdot (p_i - p_o) = 7.457 \cdot 10^{12} \cdot d_c^4 \qquad (14)$$

A minimum column plate number is required in order to obtain a sharp desorption profile. Due to the low pressure drop over the trap, the equation describing the theoretical plate height of the column for large k values can be simplified to:

$$H = \frac{2 \cdot D_m}{u} + \frac{11 \cdot d_c^2 \cdot u}{96 \cdot D_m} \qquad (15)$$

Where D_m is the diffusion coefficient of the solute in the mobile phase and u is the linear velocity of the mobile phase. In our case, the mobile phase is air. The volatile organic compounds of interest have D_m values in air of around 0.1 cm^2/s [17]. By substituting $H = L/N$ and $u = 4F/\pi d_c^2$ and some simple mathematical operations, we obtain the following equation describing the length required to obtain a plate number of 100 as a function of column diameter:

$$L = 2.433 + 942 \cdot d_c^2 \qquad (16)$$

The three equations, Eqs. (12), (14), (16) describing relationships between the column length, L, and the diameter, d_c, that a useful trap should meet are shown graphically in Fig. 3. The following numerical values are used: $F = 100$ ml/min, $p_i = 1$ bar, $p_o = 0.9$ bar, $\eta = 2 \cdot 10^{-4}$ g/cm.s, $D_m = 0.1$ cm^2/s and $N = 100$. Line 1 identifies columns with an internal volume of 2 ml. Line 2 shows columns with 100 theoretical plates at a flow-rate of 100 ml/min. Line 3 finally represents columns that give a flow-rate of 100 ml/min at an inlet pressure of 1 bar and an outlet

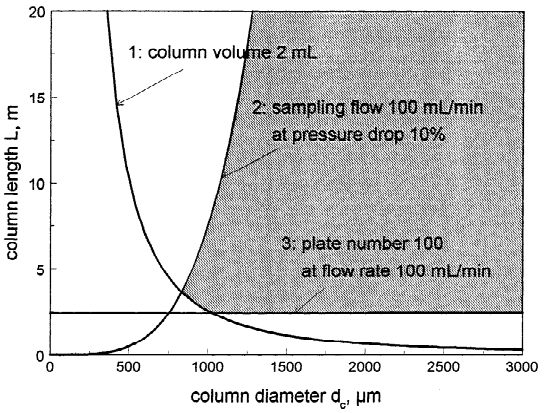

Fig. 3. Requirements for the open tubular trapping column. Columns fulfilling the requirements of having more than 100 theoretical plates, having a larger internal volume than 2 ml and allowing flow-rates higher than 100 ml/min are in the shaded area.

pressure of 0.9 bar. From this figure, it can be seen that the column of choice should be in the shaded area. Only columns with a diameter of 0.7 mm or larger can meet the requirements. These columns will have at least 100 theoretical plates, an internal volume larger than 2 ml and at the same time they will allow a sampling flow-rate that is higher than 100 ml/min at a pressure drop of 0.1 bar (10%).

3. Preliminary experiments

3.1. Experimental set-up

A series of model experiments was performed to investigate the applicability of the equilibrium preconcentration approach presented here. A schematic diagram of the set-up is shown in Fig. 4. The

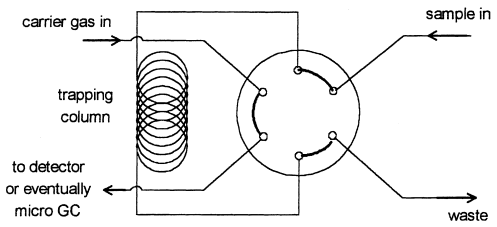

Fig. 4. Schematic diagram of the experimental set-up for the equilibrium (ab)sorption procedure.

detector used in these experiments was a flame ionization detector. The preconcentration system constructed consists of a high temperature six-port switching valve (N6WT) with a 0.010″ port diameter (VICI Valco, Schenkon, Switzerland) and a 20 m × 530 µm × 5 µm CP Sil-5 CB (Chrompack, Middelburg, Netherlands) open-tubular trapping column installed inside the oven of a Varian 3400 GC (Sunnyvale, CA, USA). Trap columns with larger diameters meeting the requirements stated in Section 2.5 were not available at the time when these experiments were carried out. In order to have a sufficient volume of the enriched gas sample, a rather long column had to be used, which precluded the use of high sampling flow-rates, due to an excessive pressure drop.

Fig. 4 shows the flow selection valve in the ''sampling'' position. The 0.010″ bore of the valve and the 20 m long, 530 µm column used here limited the sampling flow-rate to 60 ml/min without causing an excessive pressure drop. After equilibrium had been established, the valve was switched to the ''desorb–flush'' position for about 2 min, in order to purge the column with helium carrier gas to remove air. The helium flow-rate during purging was about 3 ml/min. After this, the valve was switched to the ''isolation'' position, an intermediate position between the ''sampling'' and the ''desorb–flush'' positions and the GC oven was heated to the desorption temperature. After the oven reached the desired temperature, the valve was switched to ''desorb'' and the enriched sample plug was pushed out of the column directly to a flame ionization detector by the helium carrier gas.

Gaseous standard samples of alkanes in air were generated using a laboratory-made dilution device, as described previously [2]. In this series of experiments, the air sample stream was pushed through the trapping column at a pressure of 2 bar. The inlet pressure of the helium purge/carrier gas was also set at 2 bar.

3.2. Results and discussion

Fig. 5 shows the desorption profiles of heptane (A), octane (B) and nonane (C). The adsorption temperature was 30°C, the desorption temperature was 200°C. The low plateaux at around 3, 7 and 18

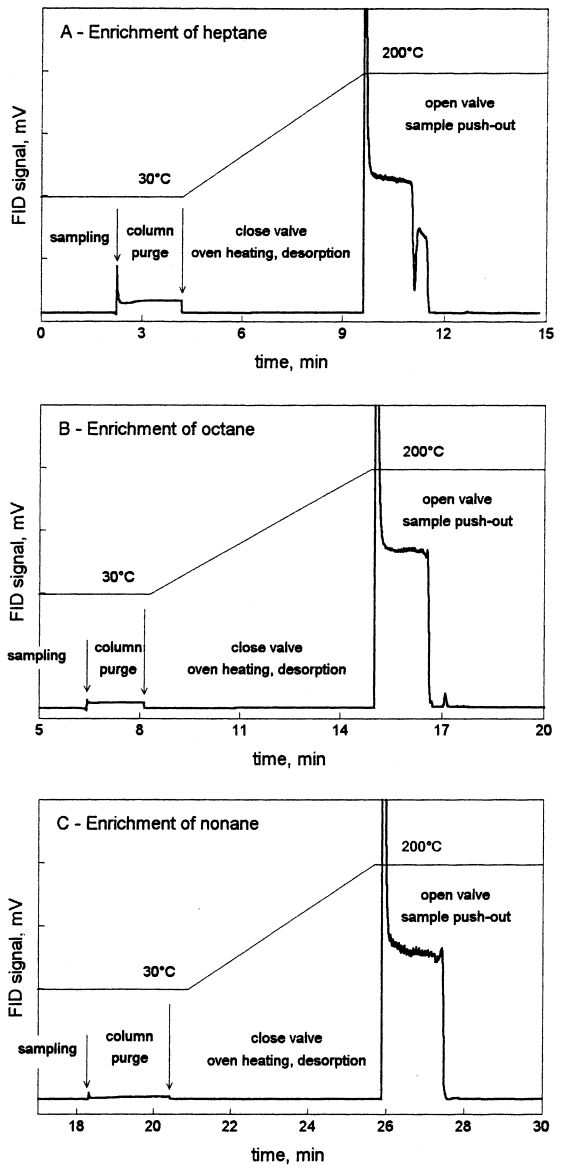

Fig. 5. Examples of the desorption profiles of alkanes using the equilibrium (ab)sorption technique.

min, respectively, show the original gas samples. The high plateaux indicate the enriched samples. The narrow peaks at the beginning of a plateau are caused by flow disturbances. A flow distortion on the mass flow-sensitive flame ionization detector results in a peak, despite the fact that the concentration is stable. The figure clearly shows that stable, enriched gas flows can be generated using the approach developed here. Depending on the conditions used and the components studied, enrichment factors of between three and sixty were found.

Table 2 shows a summary of calculated and experimentally observed capacity factors as well as enrichment factors. Calculated factors were obtained from published (α/β) and $(\Delta H/R)$ values [19]. The table shows that these values are in good agreement with the experimental data measured using conventional GC–flame ionization detection (FID). The differences sometimes observed are most likely due to small variations in the sampling and desorption flow-rates and inaccuracies in the published enthalpy and entropy values. Enrichment factors now can be predicted either directly for the calculated capacity factors or from the experimentally obtained retention data. Direct experimental measurement of enrichment factors is possible by comparing the heights of the desorption plateaux with the heights of un-enriched gas sample signals. Values of experimentally measured enrichment factors are summarized in the lower part of Table 2. Again, a good agreement with calculated values can be observed. Repeated retention time measurements, used for calculation of the capacity factors, have shown relative standard deviations (R.S.D.s) of lower than 1%. R.S.D. values of the measured enrichment factors are generally in the range of 5–8%.

As can be seen from the equations in Section 2.1, the enrichment factors strongly depend on the temperatures used for adsorption and desorption and, to a lesser extent, on the phase ratio of the column. Lower adsorption temperatures, higher desorption temperatures and lower phase ratios increase the enrichment factors substantially. The results in Fig. 5 and Table 2 clearly illustrate the potentials of this new method of gas preconcentration. Further studies will be dedicated to exploring the full potentials of the new techniques and to evaluating the coupling of the preconcentration technique described here to portable instrumentation for high-speed GC for selected applications, such as VOC analysis in air.

4. Conclusion

The study described above has demonstrated the potentials of the new preconcentration/enrichment

Table 2
Calculated and experimentally found enrichment factors of the tested *n*-alkanes

Compound	Thermodynamic term		Capacity factor				Enrichment factor		
	α/β	$\Delta H/R$	$k_{30°C}$	$k_{140°C}$	$k_{200°C}$	$k_{250°C}$	$E_{30-140°}$	$E_{30-200°}$	$E_{30-250°}$
Calculated capacity factors and enrichment factors[a]:									
n-Hexane	136.0E−6	3163	4.62	0.29	0.11	0.06	3.59	4.17	4.37
n-Heptane	67.0E−6	3680	12.54	0.50	0.16	0.08	8.39	10.81	11.65
n-Octane	34.2E−6	4179	33.14	0.84	0.23	0.10	17.97	26.85	30.11
n-Nonane	17.0E−6	4682	86.67	1.42	0.34	0.13	35.83	64.81	76.63
Measured capacity factors, calculated enrichment factors[b]:									
n-Hexane			3.75	0.23	0.15	0.06	3.05	3.26	3.53
n-Heptane			10.00	0.39	0.23	0.09	7.19	8.13	9.17
n-Octane			26.42	0.68	0.26	0.12	15.73	20.97	23.59
n-Nonane			69.71	1.13	0.41	0.19	32.73	49.44	58.60
Measured enrichment factors[c]:									
n-Hexane							3.33	3.56	3.75
n-Heptane							7.76	9.05	10.15
n-Octane							16.67	21.67	22.25
n-Nonane							36.25	52.50	61.25

[a] Capacity factors were calculated using Eq. 9, and enrichment factors using Eq. 8.
[b] Capacity factors were calculated using measured retention data: $k=(t_R-t_M)/t_M$, enrichment factors were calculated using Eq. 8.
[c] Enrichment factors were measured as the ratio of the heights of plateaux on the desorption profiles.

technique for preconcentrating gaseous samples for high-speed narrow-bore capillary GC in general or for field-portable GC instruments in particular. Because the new method generates an homogeneously enriched sample flow, a preconcentration device based on the equilibrium (ab)sorption approach is compatible with silicon-micromachined injection valves as well as other ''time-slice'' injection devices that are used in high-speed narrow-bore capillary GC, such as actuated sample valves. The large desorption gas volume that has to be transferred to the GC column in the standard ATD technique is no longer a limiting factor. The need for a refocusing step is eliminated and, last but not least, enrichment factors can be predicted in advance.

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