Novel preconcentration technique for on-line coupling to high-speed narrow-bore capillary gas chromatography: sample enrichment by equilibrium (ab)sorption, II: Coupling to a portable micro gas chromatograph

ELSEVIER

Journal of Chromatography A, 791 (1997) 187–195

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
II. Coupling to a portable micro gas chromatograph

Hai Pham Tuan[a,*], Hans-Gerd Janssen[a], Carel A. Cramers[a], Phillippe Mussche[b], Jürgen Lips[b], Nigel Wilson[c], Alan Handley[d]

[a]*Eindhoven University of Technology, Laboratory of Instrumental Analysis, P.O. Box 513, 5600 MB Eindhoven, Netherlands*
[b]*Chrompack International, P.O. Box 8033, 4300 EA Middelburg, Netherlands*
[c]*ICI Research and Technology Center, P.O. Box 90, Wilton Center, Middlesborough, Cleveland TS90 8JE, UK*
[d]*ICI Technology, Science Support Group, P.O. Box 8, Runcorn, Cheshire WA7 4QD, UK*

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

Abstract

The technique of equilibrium (ab)sorption has been proven to be a powerful method for preconcentration of gaseous samples for high-speed narrow-bore capillary gas chromatography (GC) in general and field-portable GC instruments, often referred as micro GCs, in particular. Using a simple experimental set-up equipped with an open-tubular enrichment column it is possible to produce a homogeneously enriched sample plug, allowing reproducible injections of an enriched sample into the micro GC. Using a non-polar trapping column enrichment factors found for *n*-alkanes in the range of C_7 to C_{10} ranged from 15 to 150 and agree well with calculated values. Using a highly retentive Thermocap column, the enrichment factor observed for heptane was above 500. As the use of this new preconcentration method requires only minimum modification of the micro GC, the chromatographic performance of the instrument was not compromised by direct coupling to the preconcentration device. Examples of on-line enrichment with portable micro GC analysis of VOCs from air are shown. These examples clearly demonstrate the potentials of the new method in field analysis. © 1997 Elsevier Science B.V.

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

1. Introduction

As stated in the previous article [1], the strict requirements imposed on the input band width renders on-line coupling of a preconcentration device with instrumentation for high-speed narrow-bore capillary gas chromatography (GC) an extremely difficult task. Preconcentration devices based on conventional adsorption–thermal desorption techniques cannot be directly coupled to narrow-bore GC without strict miniaturization and/or incorporation of a powerful cryofocusing step. These demands impose great difficulties in the construction of portable analytical instrumentation based on high-speed narrow-bore GC techniques.

*Corresponding author.

0021-9673/97/$17.00
PII S0021-9673(97)00770-X

Another approach, aiming to overcome the above mentioned drawbacks by the on-line generation of a flow of a homogeneously enriched gaseous sample, is the preconcentration method based on the principles of equilibrium (ab)sorption [1]. The enriched sample flow generated allows highly reproducible injections onto the narrow-bore column using the ''time-slice'' injection technique of silicon-micromachined injection valves. The theoretical aspects and the principles of this technique have been described in detail. Preliminary experiments with a mega-bore thick-film non-polar trapping column and a flame ionization detection (FID) system have given highly promising results. In this contribution the on-line coupling of this new preconcentration technique to a field-portable narrow-bore GC instrument has been realized. Different trapping columns, differing in dimension as well as in the nature and thickness of the stationary phase layer, have been evaluated. Gaseous standard samples containing *n*-alkanes C_5 to C_{10} were used. The new method has also been applied for volatile organic compound (VOC) analysis in air. The results of this work will be described in detail.

2. On-line coupling to the micro GC

2.1. Experimental set-up

A schematic diagram of the instrumental set-up used for the experiments is shown in Fig. 1. The field-portable narrow-bore GC instrument used in the present work was a CP 2002 Micro GC supplied by Chrompack International (Middelburg, Netherlands). The micro GC was equipped with a 6 m×150 μm×0.4 μm CP-FFAP column module and a 10 m×250 μm×10 μm PoraPLOT Q column module. Only the CP-FFAP column module was used in this series of experiments. In order to minimize the dead volume of the sample inlet system as much as possible, the sampling line was disconnected from the large connector where the sample flow is split for both channels and was reconnected directly to the sample outlet of the preconcentrator by means of a 1 m×530 μm empty capillary and a Valco low dead-volume connector (VICI Valco, Schenkon, Switzerland).

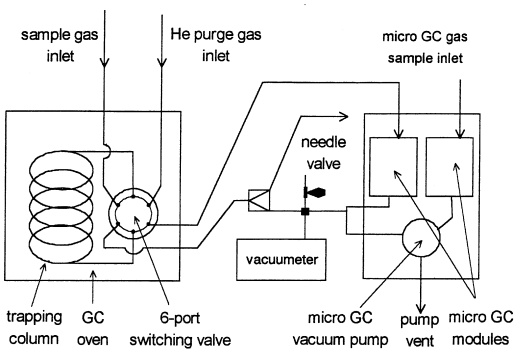

Fig. 1. Schematic diagram of the equilibrium (ab)sorption preconcentrator on-line coupled to the micro GC.

The micro GC contains a build-in vacuum pump for sampling gaseous samples into the sample loop. This vacuum pump was used to sample air through the enrichment device. To do so, a cross connector was installed in the line connecting the original sample inlet line of the micro GC and the build-in vacuum pump. A needle valve was installed in the vacuum line in order to be able to control the vacuum of the system. A flow selection valve allows switching between enrichment and sample transfer to the GC. Using the needle valve the pressure drop over the trapping column can be adjusted to the desired value. As concluded from the theoretical section of part 1 of this article, the use of outlet pressures below 900 mbar results in unstable desorption profiles [1].

The gas enrichment system, which consists of a trapping column and a high-temperature six-port switching valve was placed inside the oven of a Varian 3400 GC (Varian, Palo Alto, CA, USA), thus providing constant temperature during sampling and desorption.

The gaseous test samples were generated in a laboratory-made head-space device [2]. The liquid reservoir was filled with either pure pentane, pure heptane or a mixture of the *n*-alkanes C_7 up to C_{10}, respectively. Air was used as the dilution gas. The pressure in the vessel was maintained at 1 bar.

Three trapping columns were used in the experiments: a 5 m×530 μm×5 μm CP Sil-5 CB column, a 10 m×530 μm×20 μm Thermocap column and a 5 m×1 mm×5 μm Thermocap column. The first two column were made of fused-silica, the third one was

made from specially treated stainless-steel. All columns were supplied by Chrompack International.

2.2. Sampling and desorption procedure

Gaseous samples were pulled through the enrichment column by means of the micro GC's built-in vacuum pump. Due to software limitations, the maximum sampling time for the vacuum pump is approx. 4 min for each chromatographic run. The total sampling procedure, therefore, consisted of a series of subsequent 4 min segments. During sample enrichment, the trapping column is connected to the vacuum pump via the six-port valve (Fig. 1). After the enrichment column reached equilibrium the valve was switched, thereby allowing the helium carrier gas to purge the air our the column. Depending on the volume of the trapping column, the total purging time was 1 to 2 min.

The trapping column is then sealed by switching the six-port valve to an intermediate position. The GC oven in which the entire preconcentration system is installed, is now heated from ambient temperature to the desorption temperature (e.g., 140°C, 200°C or 250°C). After temperature had stabilized, the six-port valve is switched back to the ''inject'' position and the micro GC is programmed for a series of consecutive chromatographic runs. During each run a ''slice'' of the enriched sample plug was injected into the micro GC column. To obtain a maximum sampling frequency, the transfer line between the enrichment system and the micro GC were only shortly flushed, i.e., 1 to 5 s, prior to each injection. In the micro GC control software this is called the sampling time.

After the entire enriched sample was injected into the micro GC, the connecting capillary between the six-port valve and the sample inlet of the micro GC was disconnected to allow contaminants to be purged out of the trapping column. The GC oven could now be cooled down to the adsorption temperature preparing it for the next run.

2.3. Results and discussion

In the first series of experiments the enrichment process was monitored using the micro GC. By monitoring consecutive injections of the enriched sample, the desorption profile of the components of interest can be established simply by plotting the micro GC's thermal conductivity detection (TCD) signal for the individual components, i.e., peak areas, against the time during which chromatograms were recorded. An example of this is shown in Fig. 2. The gas eluting from the enrichment column was sampled every 40 s during desorption and the peak areas observed for a number of components were plotted versus time. These experiments were performed

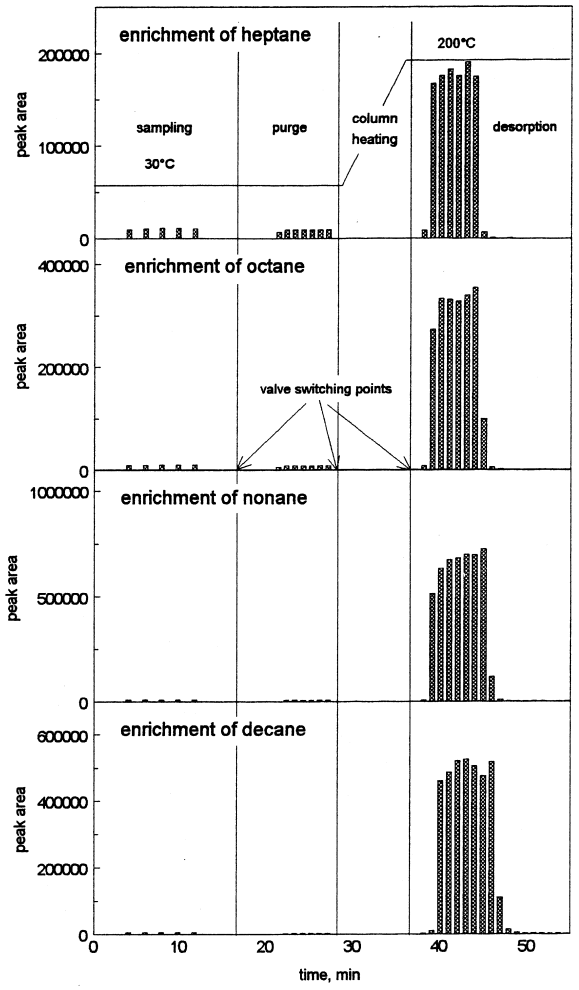

Fig. 2. Desorption profile of *n*-alkanes after equilibrium (ab)sorption enrichment on a 5 m×530 μm×5 μm CP Sil-5 CB trapping column.

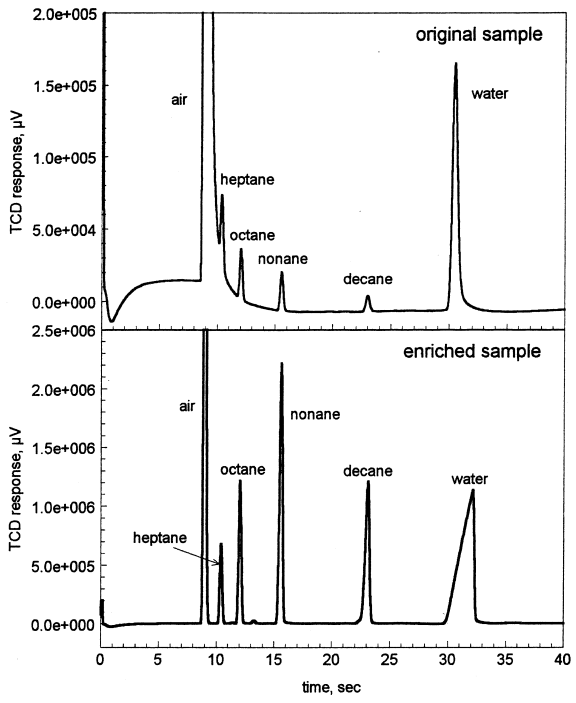

Fig. 3. Chromatograms of the gaseous samples containing *n*-alkanes, measured on a micro GC system. Chromatographic conditions: 6 m×150 μm×0.4 μm CP-FFAP column, head pressure 160 kPa, column temperature 40°C, injection time 50 ms. Upper trace: original sample, lower trace: sample after equilibrium (ab)sorption enrichment from 30°C to 200°C on a 5 m×530 μm×5 μm CP Sil-5 CB trapping column. Note the difference in the *y*-scale.

using the 5 m×530 μm×5 μm CP Sil-5 CB trapping column. 2 h were needed to equilibrate the entire column using a gaseous sample containing *n*-alkanes from C_7 to C_{10} at 30°C. As can be seen from Fig. 2, the desorption profiles of the components of interest have sharp edges and long stable regions enabling reproducible sampling onto the micro GC. The sampling time of 2 h is, however, impractically long for field operation. Chromatograms of the *n*-alkane mixture in air before and after enrichment are shown in Fig. 3. From this figure it can be seen that the water present in the sample is significantly less enriched compared to the *n*-alkanes. Hence, this proves another advantage of this technique: i.e., water is largely eliminated. Enrichment factors at different desorption temperatures are shown in Table 1. The measured values are in reasonable to good agreement with the values calculated from published entropy and enthalpy data (viz. Part 1: Principles and Theoretical Aspects [1]).

Although the above mentioned experiments have clearly proven that the preconcentration method works perfectly according to expectations, the technique still has many points that need to be improved. First of all higher enrichment factors are required. Furthermore the sampling time should be reduced. These two parameters are closely interrelated. In order to have a high enrichment factor the trapping column must exhibit a strong retention for the component of interest at ambient sampling tempera-

Table 1
Calculated and experimental enrichment factors of the selected *n*-alkanes on the 5 m×530 μm×5 μm CP Sil-5 CB trapping column

Compound	Enrichment factor		
	$E_{30-140°C}$	$E_{30-200°C}$	$E_{30-250°C}$
Calculated values			
n-Heptane	8.4	10.8	11.7
n-Octane	17.9	26.9	30.1
n-Nonane	35.8	64.8	76.6
n-Decane	48.6	109.9	143.5
Experimentally found values using the micro GC–TCD system			
n-Heptane	10	15	15
n-Octane	20	33	30
n-Nonane	40	75	71
n-Decane	65	110	150

ture. A column with a higher retention power, however, requires a longer equilibration time unless the column dimension, i.e., the column inner diameter and length, are changed facilitating higher sampling flow-rates. At the same time all extra-column flow resistance, e.g., tubing and valves, have to be reduced to an absolute minimum.

To increase the enrichment factors, a trapping column with a much more retentive stationary phase, a 5 m×530 μm×5 μm Thermocap column, was used. The enrichment of a gaseous sample consisting of heptane in air is shown in Fig. 4. From this figure it can be seen that heptane starts to break through and approach equilibrium only after 9 h sampling. The sampling flow-rate was 5 ml/min which was the maximum that could be used due to pressure drop limitations. Column equilibration with heptane required 11 h! The flat plateaus in the upper figure indicate the signal of the original sample. From the signal obtained during desorption (see lower trace in Fig. 4) the enrichment factor of heptane can be estimated. Enrichment at 50°C followed by desorption at 140°C results in an enrichment factor of approx. 500. This value is, surprisingly, about eight-times higher than the value calculated from the capacity factors at the respective temperatures indicating that a mechanism different from a pure partitioning principle might apply here.

The Thermocap stationary phase, hence, appears very attractive for preconcentrating volatile components due to its extremely strong retention. The sampling time can be reduced to acceptable levels by applying higher sampling flow-rates through wider-bore capillary columns. Using a 2 m×1 mm×5 μm Thermocap trapping column, the sampling time of heptane could be reduced to approx. 2 h. The desorption profile of heptane with the latter column is depicted in Fig. 5. Compared to the desorption profile from Fig. 4, it is obvious that the enriched sample plug is now less sharp rendering a more careful selection of the ''slice'' to be injected into the micro GC necessary. This is due to the lower plate number of the mega-bore trapping column.

The sampling time can be further shortened by reducing every possible flow resistance in the sampling line. The current six-port switching valve with 0.4 mm bores was replace by a 0.7 mm bore valve. The length of the connecting tubing was reduced to a minimum. After all modifications, equilibration of the 2 m×1 mm×5 μm Thermocap column could be completed within 50–60 min. A further reduction in sampling time could be achieved by using a shorter column, i.e., 1 m instead of 2 m. Even with the 1 m

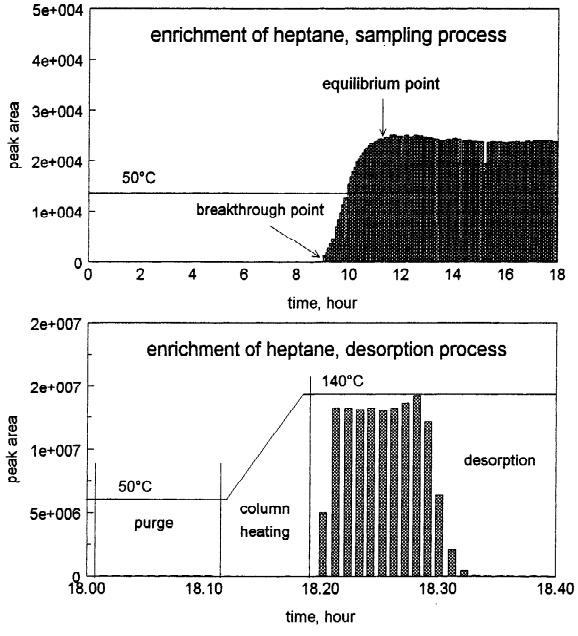

Fig. 4. Time-dependent response of heptane measured on the micro GC during equilibrium (ab)sorption enrichment process. The trapping column used was 5 m×530 μm×10 μm Thermocap. Sampling temperature was 50°C, desorption temperature was 140°C.

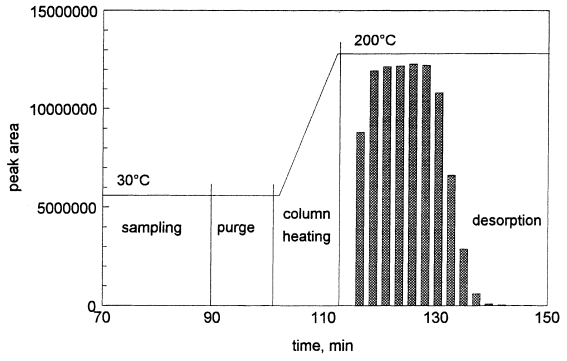

Fig. 5. Desorption profile of heptane during equilibrium (ab)sorption enrichment using a 2 m×1 mm×5 μm Thermocap stainless-steel trapping column. Sampling 90 min at 30°C, desorption at 200°C.

column the enriched gas volume obtained was sufficient for thorough flushing of the inlet line of the micro GC.

As stated above, however, the most effective way to reduce the time required for equilibration of the trap is to choose proper enrichment factors for the components of interest. In order to obtain detection limits in the ppb range, enrichment factors of, say, 500 must be achieved as the detection limits of a stand-alone micro GC are generally approx. 1–2 ppm. According to the equation for the enrichment factor we have derived in Part 1 and assuming the trapping column has a void volume of 1 ml and an infinite plate number, at least 500 ml of gas must be drawn through the column before equilibrium is established. Because of its low plate number the trapping column used in the experiments can be equilibrated only when sampling is continued far beyond the breakthrough point. This means that practically in this case a sample volume of some 1000 ml is necessary. At a sampling flow-rate of 100 ml/min, ca. 10 min is needed for the sampling process. The simple consideration presented above demonstrates how closely the two parameters sampling time and enrichment factor are interrelated. An unnecessarily high enrichment factor will result in excessively long sampling times which are not acceptable for fast GC procedures. Sampling times of less than 20 min can be considered to be feasible. In order to achieve this goal all parameters such as for example type of stationary phase and sampling temperature, must be carefully optimized. This is the main aim for future research work.

3. Application in VOC analysis

To demonstrate the potentials of the new preconcentration technique in field applications, it was applied for the analysis of VOCs in air. A 1 m×1 mm×5 μm Thermocap column was used for these experiments.

Two VOC mixtures in air were generated. The first mixture contained benzene, toluene and *p*-xylene (BTX) and was prepared by diluting a standard mixture of these components in helium (25 ppm each) with air in an exponential dilution device. The concentrations of the individual components in the final gas sample was approx. 1 ppm. The free fatty acid phase (FFAP) column module of the micro GC was used to analyze the gas samples. Chromatograms of this gas mixture before and after enrichment, recorded with the micro GC, are shown in Fig. 6. The sampling process was completed in 3 h at a sampling flow-rate of 150 ml/min. The fronting peaks for toluene and *p*-xylene in the lower trace are obviously caused by the narrow-bore FFAP column being overloaded. Enrichment factors of the individual components are summarized in Table 2. Detection limits of 1–2 ppb can be achieved for benzene and toluene. *p*-Xylene, with its extremely high enrichment factor, can be detected at even lower concentration level, i.e., 0.5 ppb.

Other gas samples containing some seven VOCs in air were generated in a laboratory-made head-space device. The reservoir of the device was filled with a liquid mixture of VOCs consisting of methyl bro-

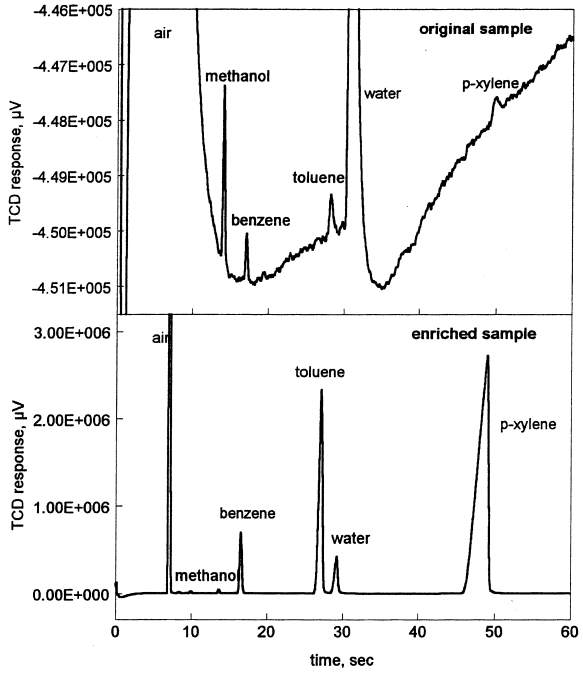

Fig. 6. Enrichment of a gaseous sample containing benzene, toluene and *p*-xylene in air using the equilibrium (ab)sorption method. Chromatographic conditions: micro GC 6 m×150 μm×0.4 μm CP-FFAP column, column head pressure 200 kPa, column temperature 40°C. Trapping column 1 m×1 mm×5 μm stainless-steel Thermocap, sampling temperature 30°C, desorption temperature 200°C. Note the difference in the *y*-scale.

Table 2
Enrichment factors of selected VOCs using a 1 m×1 mm×5 μm Thermocap trapping column

Compound	b.p. (°C)	Enrichment factor at		
		150°C	200°C	250°C
Benzene	80.1		570	
Toluene	110.6		2100	
p-Xylene	137.5		17 000	
Methylbromide	3.6	11	17	21
Dichloromethane	39.8	71	96	101
trans-1,2-Dichloroethene	47.2	109	151	124
1,1,2-Trichlorotrifluoroethane	46.0	139	269	391
1,1-Dichloroethane	57.3	144	258	360
Chloroform	61.5	207	366	452
1,1,1-Trichloroethane	74.1	386	968	1570

mide, dichloromethane, *trans*-1,2-dichloroethene, 1,1,2-trichlorotrifluoroethane, 1,1-dichloroethane, chloroform and 1,1,1-trichloroethane. The diluting air flow was set at different values in order to generate gas samples at various concentration levels ranging from approx. 0.05 to 5 ppm. The chromatogram of the gas sample with the lowest concentration level, i.e., 0.05 ppm, after enrichment is shown in Fig. 7. For the analysis of highly volatile components the PoraPLOT column module of the micro GC was used in this series of experiments. The enrichment factors of these VOCs at different desorption temperatures are listed in Table 2. With the relatively low enrichment factors to be achieved the sampling time was only 30 min, much shorter than in case of the above mentioned BTX mixture. The estimated detection limits are in the range of 5–10 ppb.

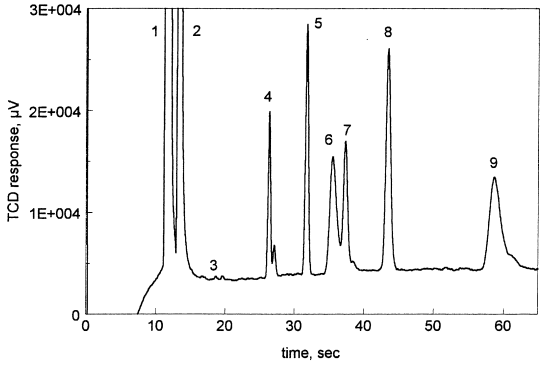

Fig. 7. Chromatogram of an enriched gas sample containing some seven VOCs in air at a concentration level of ca. 50 ppb using the equilibrium (ab)sorption technique. Elution order: 1=air, 2=water, 3=methyl bromide, 4=dichloromethane, 5=*trans*-1,2-dichloroethene, 6=1,1,2-trichlorotrifluoroethane, 7=1,2-dichloroethane, 8=chloroform and 9=1,1,1-trichloroethane. Chromatographic conditions: micro GC 10 m×250 μm×10 μm PoraPLOT Q column, head pressure 310 kPa, temperature 180°C. Trapping column 1 m×1 mm×5 μm stainless-steel Thermocap, sampling temperature 30°C, desorption temperature 250°C.

The peak areas of the enriched components at different concentration levels were processed with the least square linear regression technique. Parameters of the regression equations are summarized in Table 3. These graphs show a good linearity which indicates that in the evaluated concentration range the (ab)sorption of an individual component is not affected by the presence of other components. This is in agreement with what one would expect for a true sorptive enrichment.

4. Evaluation of other trapping columns

4.1. Experimental

Apart from the mega-bore thick-film non-polar capillary columns and the Thermocap trapping column described above, two other types of trapping columns were investigated. The first column studied was a 15 m×530 μm×20 μm PoraPLOT S column (Chrompack). The second column was a laboratory-made column, consisting of a 30 cm×1.8 mm stainless-steel tube that contained a 30 cm piece of 2 mm O.D.×1 mm I.D. silicone tubing (abbreviated as the stainless steel–silicone tube). The silicone tubing was fitted snugly inside the stainless-steel tube with no free outer space and, hence, formed a sort of

Table 3
Parameters of the regression equations: peak areas vs. concentrations

Compound	Intercept (peak area unit)	Slope (area unit/ppm)	Correlation coefficient
Bromomethane	50	1048	0.9953
Dichloromethane	952	94 224	0.9989
trans-1,2-Dichloroethene	1895	166 598	0.9986
1,1,2-Trichlorotrifluoroethane	−8074	210 179	0.9997
1,1-Dichloroethane	−2086	145 303	0.9994
Chloroform	4770	232 413	0.9987
1,1,1-Trichloroethane	1965	251 248	0.9993

The VOCs in a air sample were enriched using the equilibrium (ab)sorption technique. Chromatographic conditions: micro GC 10 m×250 μm×10 μm PoraPLOT Q column at 310 kPa and 180°C. Trapping column 1 m×1 mm×5 μm stainless-steel coated with Thermocap, sampling temperature 30°C, desorption temperature 250°C.

thick-film silicone stationary phase. The gas sample flows exclusively through the inner space of the silicone tubing.

For the testing of the PoraPLOT S column the FID system of the Varian GC was used. The experimental set-up was thus similar as in the preliminary experiments with the mega-bore non-polar columns described in Part 1: Principles and Theoretical Aspects [1]. The performance of the laboratory-made silicone-filled tube was monitored using the micro GC.

All experiments were performed using a stream of gaseous sample of pentane in air which was generated in a laboratory-made dynamic head-space device [2].

4.2. Results and discussion

Fig. 8 shows the desorption profile of pentane from the PoraPLOT S column. Despite the long sampling time of over 2 h full equilibration of the column had not yet been achieved. The FID signal of pentane, eluted long after the dead time which is around 1 min, clearly shows a partial adsorption. The solid adsorption material appears to show strong adsorption, even for the relatively volatile pentane. The component enrichment factor was found to be very high, approx. 400. Although the plateau has a stable average value, relatively large fluctuations compared to FID desorption profiles generated on other trapping columns (viz. [1]) can be seen. They are most likely caused by the heterogeneity of the porous adsorption layer deposited on the wall of the column. This might lead to poorly reproducible enrichment factors when PoraPLOT columns is used to enrich gaseous samples for the micro GC.

The desorption profile of heptane obtained on the laboratory-made stainless-steel–silicone tube is shown in Fig. 9. Compared to the other trapping columns the sampling time on this tube was shortened considerably. Equilibration with pentane was achieved in about 5 min. This is clearly due to the larger diameter of the tube, its shorter length and last but not least the weaker retentive strength. As this system is basically a liquid stationary phase column, the enrichment factors can be predicted using the theoretical considerations presented in the previous article [1]. The large tail of the desorption band and the lack of a flat plateau, however, indicate that the tube has too low a theoretical plate number. This most likely is caused by the very high ''film-thick-

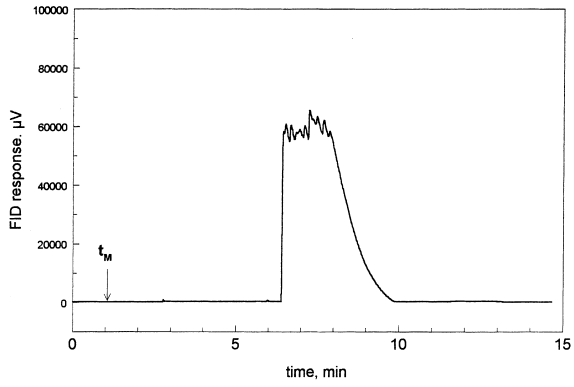

Fig. 8. Desorption profile of pentane after equilibrium (ab)sorption enrichment process on a 20 m×530 μm×20 μm PoraPLOT S column. Sampling time 2 h, sampling temperature 30°C, desorption temperature 200°C.

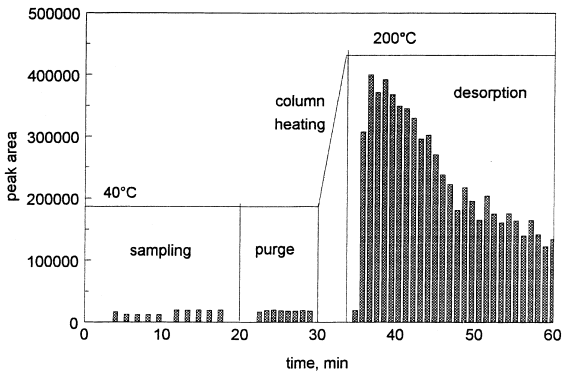

Fig. 9. Desorption profile of pentane from a laboratory-made 30 cm×1.8 mm×0.9 mm stainless-steel–silicone tube. Sampling time 20 min, sampling temperature 40°C, desorption temperature 200°C.

ness'', which was almost 1 mm, together with the short length of only 30 cm.

5. Conclusions

The experimental results described above clearly show the compatibility of preconcentration techniques based on the equilibrium (ab)sorption principle with high-speed narrow-bore GCs, at least in terms of chromatographic performance. Further study of its applicability will focus on reducing the sampling time to the 10–20 min range. In case of field-portable micro GCs no major modification of the micro GC hardware is required. The chromatographic performance of the GC instrument, therefore, is not compromised. Experiments with gas samples containing *n*-alkane mixtures showed very good results with favorable enrichment factors. The enrichment factors measured on trapping columns with 100% methylsilicone stationary phases agree well with calculated values. Due to the weak retention of the methylsilicone stationary phase, however, rather low enrichment factors are obtained. For volatile components such as VOCs with boiling points in the range of 40°C–100°C a more retentive Thermocap stationary phase could be used in order to obtained acceptable enrichment factors and correspondingly low detection limits, i.e., in a low ppb level. Benzene and toluene can be detected at 1–2 ppb level. The detection limit of *p*-xylene can be as low as 0.5 ppb. Components with lower boiling points will need a stationary phase with even stronger retention, e.g., a PoraPLOT column. The weak silicone liquid stationary phase could provide good enrichment for components with higher boiling point range. In order to achieve the short sampling times required in field operations trapping columns with a large inner diameter (1–2 mm) should be used. All extra-column flow resistance must be also reduced to an absolute minimum.

References

[1] H. Pham Tuan, H.-G. Janssen and C.A. Cramers, J. Chromatogr. A 791 (1997) 177.
[2] H. Pham Tuan, H.-G. Janssen, E.M. Kuiper-van Loo, H. Vlap, J. High Resolut. Chromatogr. 18 (1995) 525.