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Solvent elimination rate in temperature-programmed injections of large sample volumes in capillary gas chromatography☆

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ABSTRACT

Temperature-programmed sample introduction is a very useful approach for the injection of large sample volumes in capillary gas chromatography and also holds promise for liquid chromatography–gas chromatography coupling The optimization of a temperature-programmed injector for both these applications depends on numerous factors such as sample volume, liner design and temperature, speed of sample introduction and purge gas flow-rate The maximum allowable speed of introduction of large sample volumes with simultaneous elimination of the solvent is determined by the solvent elimination rate A theoretical model is proposed to predict an optimum combination of the speed of sample introduction, the initial liner temperature and the purge gas flow-rate The validity of the model is discussed and evaluated The solvent elimination rate is shown to depend on, amongst others, the vapour pressure of the solvent, and can be increased by an increase in the purge gas flow-rate and/or by a decrease in the inlet pressure The observed cooling effect and the effect of the design of the liner on the solvent elimination rate are emphasized

INTRODUCTION

Temperature-programmed sample introduction (also known as PTV injection), proposed by Abel [1] in 1964, was developed and applied for the introduction of large sample volumes (up to 20 μl) in biomedical (steroids) and environmental (pesticides) applications by Vogt and co-workers in 1979 [2–4] Vogt and co-workers showed that the method allowed the simultaneous elimination of the solvent and selective trapping of components with a much lower volatility in the cold liner, prior to splitless transfer of the deposited fraction of the sample into the column by rapid temperature-programmed heating Temperature-programmed sample introduction offers many advantages in comparison with hot injection methods In 1981 Schomburg [5] and Poy *et al* [6] showed that cold split or splitless injection greatly reduced the discrimination of less volatile components Their observations were confirmed by others [7–15] The quantitative performance of the PTV injection system appears to be

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comparable to that of on-column injection [9–11, 14–18] The negative effect of column contamination due to the presence of residue components in the sample in on-column sample introduction can be greatly avoided with temperature-programmed sample introduction [18–20]

The potential and limitations of temperature-programmed sample introduction with solvent elimination have hardly been studied so far Some incidental trial on the optimization of this technique were reported by Herraiz and co-workers [21–23] and Termonia *et al* [24]

Further investigations of the effects of important factors such as injection temperature, injection speed, split flow, purge time, design of the liner and the nature of the solvent on the recoveries of the components of interest are required for a proper judgement of the applicability of the temperature-programmed injector for the introduction of large sample volumes in capillary gas chromatography (GC) and to establish its potential as an interface in coupled liquid chromatography (LC)–GC

In this paper we present a method that allows the calculation of the solvent evaporation rate in the liner of a temperature-programmed injector Further, we discuss the effects of various operating conditions on the solvent elimination process

EXPERIMENTAL

Instrumentation

A Model HP 5890 gas chromatograph (Hewlett-Packard, Avondale, PA, USA) equipped with a flame ionization detector and provided with a Model HP 3393A integrator and a Type KAS 502 temperature-programmed injection system (Gerstel, Mulheim a/d Ruhr, Germany) was used Sample introduction was done either by means of an autosampler (Model HP 7673, Hewlett-Packard) or a syringe pump Two different syringe pumps were used The Type MF-2 "micro feeder" syringe pump (Azumadenkikogyo, Japan) allowed sample introduction with a speed corresponding with micro-bore LC mobile phase flow-rates Using this system the speed of sample introduction could be varied between 0 7 and 83 3 μl/min A microprocessor-controlled syringe pump (Digisampler, Gerstel) allowed the injection of defined volumes of samples up to 1000 μl with a speed between 1 and 2000 μl/min The sample supplied by the syringe pump was transferred directly to the injector via a fused-silica or a metal capillary

For temperature measurements inside the liner during solvent elimination a Type 870 digital thermometer (Keithley, USA) with a Type 8701 thermocouple adapter was used Temperature changes were recorded on a BD-40 recorder (Kipp & Zonen, Delft, Netherlands) The temperature was measured at three different positions in the liner at 15, 35 and 55 mm below the injection point, which coincides with the top of a 13-mm glass-wool plug inside the liner

Operating conditions

Helium was used as the carrier gas at an inlet pressure of 100 kPa (linear gas velocity $\approx$ 60 cm/s) Selective solvent elimination was performed either at the normal carrier gas inlet pressure or at a reduced inlet pressure of 5–20 kPa The purge gas flow-rate was varied between 210 and 620 ml/min The sequence of events during sample introduction, solvent elimination and sample transfer is depicted schematically in Fig 1 The split valve was open

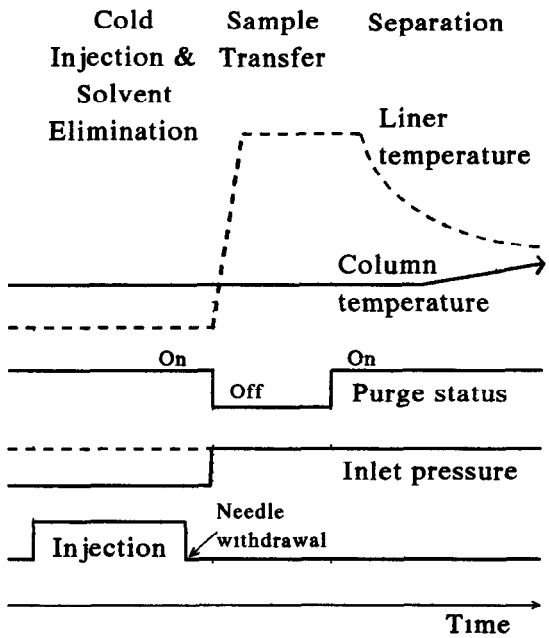

Fig 1 The sequence of events during sample introduction, solvent elimination and sample transfer

during the injection period and an additional time of 10–60 s (the additional purge time) Thereafter, simultaneously the inlet pressure was increased to 100 kPa (only if the introduction and solvent elimination were performed at decreased inlet pressure), the split valve was closed, the temperature programme of the column was started and the injector was heated to its final temperature (300°C) with a heating rate of 12°C/s The injection system was kept at this temperature for 1–3 min and then cooled to 50–60°C

For the GC separation, two 25 m × 0 32 mm I D non-polar fused-silica capillary columns (Chrompack, Middelburg, Netherlands) were used Column A was coated with CP-Sil 5 and had a film thickness of 2 33 μm and column B was coated with CP-Sil 5 CB and had a film thickness of 1 21 μm The GC oven temperature programme for column A was initial temperature 40°C for 4 min (isothermal), then increased at 10°C/min to 140°C and at 15°C/min to 250°C (held for 10 min isothermal) In the experiments with column B the initial temperature was 40°C (2 min isothermal) and was then increased at 10°C/min to 280°C

Test mixtures

Synthetic standard mixtures were prepared that contained *n*-alkanes (C_9–C_{20}) and components of different polarity and volatility The concentrations of the solutes in samples A and B and the retention times of the components on columns A and B, respectively, under standard operating conditions are given in Table I Freshly distilled *n*-hexane was used as the solvent for preparing the standard samples and for subsequent dilution of the samples

Procedure for calculation of recoveries

Normalized peak areas (expressed in area counts per ng of injected component) were used for recovery calculations throughout As a reference, standard normalized peak areas were used, which were determined by the cold splitless injection of 1 μl of the standard solution The amounts of components introduced into the columns correspond to 20–40 ng

TABLE I

SYNTHETIC STANDARD SAMPLES

Compound	Sample A		Sample B	
	Concentration (ng/μl)	Retention time[a] (min)	Concentration (ng/μl)	Retention time[b] (min)
n-Nonane	35 1	11 85	10 9	7 55
2-Octanone	41 0	13 41	10 7	8 92
n-Decane	28 0	14 01	11 4	9 48
2,6-Dimethylphenol	31 5	15 75	10 5	10 98
2,6-Dimethylaniline	31 6	16 76	12 1	11 98
n-Dodecane	22 6	17 50	11 3	12 94
1-Aminodecane	39 2	18 03	–	–
n-Tridecane	23 4	18 83	10 5	14 50
(–)-Nicotine	42 4	19 43	10 9	14 97
n-Tetradecane	23 8	20 02	11 5	15 96
2-Tridecanone	28 0	20 94	10 1	17 06
Fluorene	23 2	22 29	–	–
n-Hexadecane	–	–	10 8	18 66
n-Heptadecane	24 6	23 20	11 7	19 89
n-Octadecane	26 6	24 38	9 1	21 07
Anthracene	26 2	24 90	–	–
Methyl palmitate	21 0	25 95	10 3	22 29
n-Eicosane	27 4	27 47	9 3	23 25

[a] On column A under standard operating conditions
[b] On column B under standard operating conditions

per compound for sample A and to about 10 ng per compound for sample B

Liner design

Three different liners were used (Fig 2) (1) an empty, baffled liner, (2) a baffled liner with a plug (length 13 mm) of silanized glass-wool in the upper part, and (3) a straight liner packed with silanized glass-wool (plug length 40 mm)

THEORETICAL

Selective solvent elimination is an attractive way to introduce large amounts of dilute samples into a capillary GC column Independent of the method used for this purpose (retention gap with or without so-called concurrent solvent evaporation, cold trapping, temperature-programmed injection or a combination of these techniques), the speed of sample introduction and the rate of solvent elimination have to be matched

The saturated vapour volume (V_g) at a given temperature (T), which corresponds to a defined liquid volume (V_l), can be calculated according to the following equation

$$V_g = \frac{V_l \rho R T}{M p_j} \quad (1)$$

where ρ = density of the solvent, M = molecular weight of the solvent, R = gas constant and p_j = partial pressure of the solvent In deriving this equation it is assumed that the solvent vapour exhibits ideal gas behaviour Fig 3 shows the calculated saturated vapour volumes as obtained from eqn 1 for a number of different solvents These values show the minimum volume of gas required to

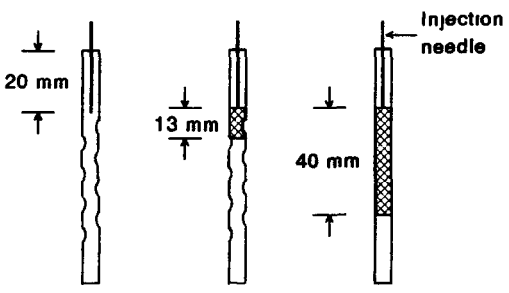

Fig 2 Schematic design of the liners Hatched part silanized glass-wool, liner length 92 mm, I D 1 3 mm

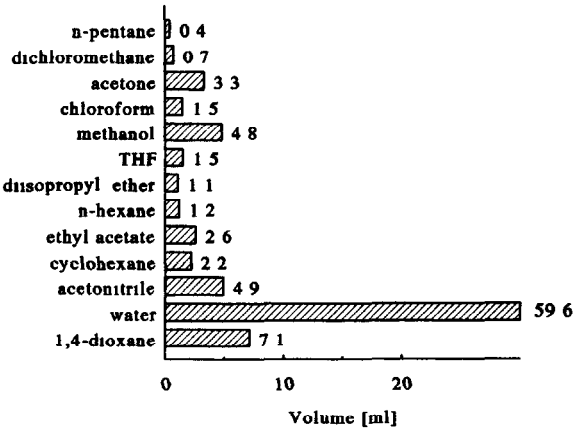

Fig 3 Saturated vapour volumes of 1 μl of different solvent at 20°C

remove the solvent as vapour from the liner The values of the partial pressures of the solvents were calculated from Antoine's equation [25] The saturated vapour volumes of different solvents at 20°C vary between 0 4 ml for *n*-pentane and 60 ml for water For very polar solvents, *e g* , methanol, acetonitrile and water used in reversed-phase liquid chromatography, the vapour volumes ar much larger than for non-polar or medium polarity solvents with similar boiling points

During the introduction of large sample volumes the speed of sample introduction into the liner of the injector should not exceed the solvent elimination rate In the steady state the mass flow of liquid solvent entering the liner (or interface) equals the mass flow of the corresponding solvent vapour at the exit of the liner, *i e* , the amount of liquid solvent in the liner remains constant Assuming isothermal evaporation conditions and further assuming that the gas leaving the liner is saturated with solvent vapour, the maximum injection speed which equals the solvent elimination rate can be calculated as follows

$$V_{inj,max} = V_{el} = \frac{M p_j}{\rho R T_o} \frac{p_o}{p_i} V_{t,o} \quad (2)$$

where $V_{inj,max}$ = maximum speed of sample introduction, V_{el} = solvent elimination rate, $V_{t,o}$ = total gas flow-rate at outlet conditions (T_o and p_o) and p_i = inlet pressure of the liner

Eqn 2 indicates that the solvent evaporation rate

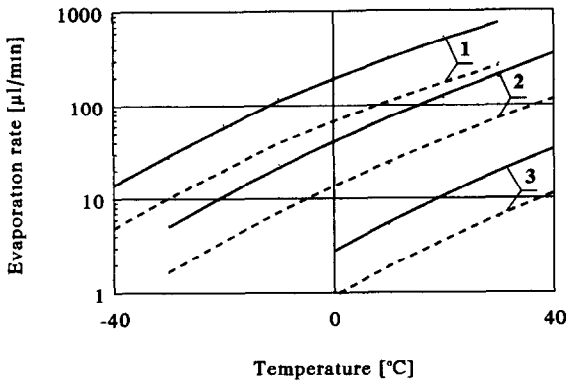

Fig 4 Dependence of the evaporation rate on the initial liner temperature at different gas flow-rates (dashed lines, 210 ml/min, solid lines, 620 ml/min) for (1) hexane, (2) methanol and (3) water Values calculated for $p_o/p_i = 1$

is proportional to the gas flow-rate in the liner given by $V_{t\,o}p_o/p_i$ Therefore, reducing the pressure in the liner and/or increasing the total gas flow-rate increases the solvent evaporation rate The influence of the liner temperature on the evaporation rate is illustrated in Fig 4 for hexane, methanol and water A temperature increase of 10°C increases the evaporation rate by a factor of 1 5–2

The approach described above permits the calculation of the elimination rate and, hence, the maximum acceptable speed of sample introduction as a function of the liner temperature and the purge gas flow-rate for various solvents In deriving this equation it is assumed that the evaporation process takes place under isothermal conditions and that the purge gas is saturated by solvent vapour

RESULTS AND DISCUSSION

In temperature-programmed introduction of large sample volumes in capillary GC and in on-line LC–GC, two main steps can be distinguished In the first step a liquid sample is introduced into the liner of the injector The solvent is selectively eliminated during introduction while less volatile compounds are retained in the liner In the second step the compounds trapped in the liner are transferred splitlessly into the column In the first step, in which selective preseparation occurs, the PTV injection of large sample volumes has to be optimized with respect to solvent elimination and component recovery For this optimization the following factors need to be taken into account design of the liner, inlet pressure, initial liner temperature, purge flow, speed of sample introduction, additional purge time, sample volume and physico-chemical properties of the solvent

The effect of differences in the liner design on the solvent elimination process can be demonstrated by comparing the total amounts of solvent introduced into the column (Table II) after solvent elimination It should be noted that this amount of solvent consist partly of solvent introduced into the column during split solvent elimination and partly of residual solvent retained in the liner after the solvent elimination process The solvent retained in the liner is transferred into the column in the splitless mode together with compounds of interest trapped in the liner during solvent elimination When a sample of 5 6 µl is introduced into the PTV liner at an initial liner temperature of −30°C in the solvent elimina-

TABLE II

EFFECT OF DIFFERENCES IN THE LINER DESIGN ON TOTAL AMOUNT OF SOLVENT ENTERING THE COLUMN

Operating conditions purge gas flow-rate, 210 ml/min, additional purge time, 45 s, inlet pressure, 100 kPa

Operating conditions	Amount of solvent (µl)		
	Liner 1	Liner 2	Liner 3
Sample volume 5 6 µl, injection time 40 s, initial liner temperature −30°C	2 7	0 5	0 2
Sample volume 21 µl, injection time 75 s, initial liner temperature −20°C	2 8	1 1	0 5

tion mode, the amounts of solvent introduced into the column correspond to about 2 7 μl, 0 5 and 0 2 μl of hexane for liners 1, 2 and 3, respectively From these results it can be concluded that the solvent elimination rate for liner 1 is low, it is estimated to be about 2 μl/min For liners packed with glass-wool the solvent elimination rate is increased significantly, corresponding to about 3 5 μl/min for liner 2 and about 4 μl/min for liner 3 These values are lower than the evaporation rates calculated according to eqn 2, where it was assumed that instantaneous saturation of the purge gas with solvent vapour occurs From the differences between the calculated and the experimental data it can be concluded that the purge gas is not fully saturated with solvent vapour When larger samples of 21 μl were introduced at an initial liner temperature of −20°C, liner 1 again appeared to be less effective than the liners packed with glass-wool These results indicate that the degree of saturation increases when the gas–solvent contact area in the liner is enlarged Packing the liner with glass-wool appears to be an efficient means of increasing the contact area Consequently, it can be expected that any modification of the liner which results in an increased gas–solvent contact area will be beneficial for the rate of solvent evaporation and, hence, the analysis time

The solvent evaporation rate, as it is proportional to the ratio of the outlet to the inlet carrier gas pressure (see eqn 2), can be increased by decreasing the pressure in the liner Additionally, at a lower column inlet pressure the splitting ratio will increase, because the gas flow through the liner is mass-flow controlled and the column flow is pressure controlled (back-pressure control) A reduced amount of solvent will enter the column during split solvent venting at low column inlet pressures This is demonstrated in Fig 5 The shaded peaks represent the total amount of solvent entering the column When large sample volumes of 1000 μl were injected (Fig 5A and B), the amounts of solvent introduced into the column at the maximum obtainable purge gas flow-rate (*ca* 600 ml/min) correspond to about 9 and 0 5 μl at inlet pressures of 100 and 18 kPa, respectively At a lower purge gas flow-rate (210 ml/min) and for sample volumes of 250 μl (Fig 5C and D), the amounts of solvent introduced into the column correspond to *ca* 6 and 0 1 μl of hexane at

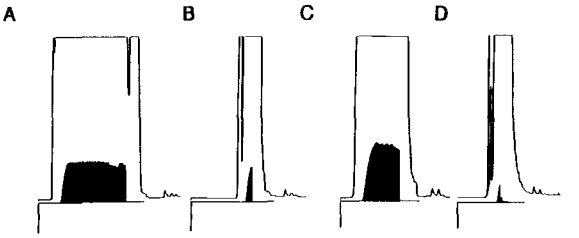

Fig 5 Effect of inlet pressure on the size of the solvent peak Operating conditions inlet pressure, 100 kPa for chromatograms A and C, 18 kPa for B and 7 kPa for D, initial liner temperature, 30°C, additional purge time, 10 s, shaded solvent peaks at attenuation = 2^{16} For more information, see text

inlet pressures of 100 and 7 kPa, respectively This means that by using reduced inlet pressures during solvent elimination the total fraction of solvent that enters the column is reduced to less than 0 05% This is a considerably smaller amount than at normal column inlet pressures Experiments showed that the stepwise increase in the pressure after solvent elimination to higher pressures during analysis does not affect the retention times of the solutes in temperature-programmed separations

Unexpectedly, it was observed that extremely low recoveries were obtained when large sample volumes were injected at a sampling speed close to the maximum acceptable speed of sample introduction predicted according to eqn 2 The results were significantly improved by a decrease in the speed of sample introduction and also in the sample size The effect of the speed of sample introduction on recovery is illustrated in Fig 6 for components with retention times between those of C_{16} and C_{20} The calculated maximum allowable speed of sample introduction predicted by eqn 2 under the given experimental conditions (purge gas flow-rate = 620 ml/min and initial liner temperature = 30°C) is *ca* 700 μl/min As the evaporation is an endothermic process, it can be expected that the temperature in the PTV liner will decrease significantly during solvent evaporation A temperature decrease in the liner would result in a reduction in the solvent evaporation rate and might easily lead to the accumulation of an excessive amount of liquid in the liner In this event, part of the introduced liquid sample will leave the liner in the liquid state via the split vent (right-hand part of Fig 6), which will lead to a loss of components and incomplete recoveries

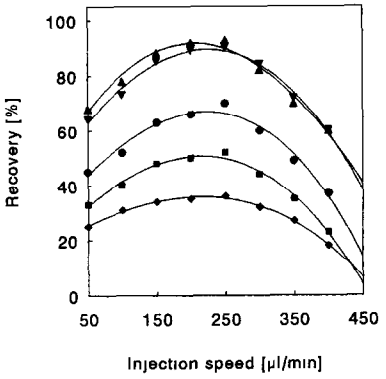

Fig 6 Influence of injection speed on the recovery of (▼) eicosane, (▲) methyl palmitate, (●) octadecane, (■) heptadecane and (◆) hexadecane Operating conditions sample volume, 250 µl, initial liner temperature, 30°C, purge gas flow-rate, 620 ml/min, inlet pressure, 18 kPa, additional purge time, 10 s, liner 2

Flooding of the liner explains the poor recoveries at high sample introduction speeds On the other hand, at too low a speed of sample introduction no liquid film is formed in the liner In the absence of such a liquid film the solutes are only weakly retained and might easily escape with the huge flow of purge gas (left-hand part of Fig 6) Probably the formation of a liquid film is essential for the selective retention of the components, because this liquid will strongly incraese the retentive power of the liner Packing of the liner with a packing material or coating of the liner with a liquid layer are possible alternatives for a selective increase in the retention of the analytes

The changes in temperature at different positions inside the liner during solvent elimination are shown in Fig 7 These changes decrease from the top to the bottom part of the liner and they depend strongly on the injection speed Obviously, the cooling effect due to vaporization of the sample is compensated for by heat transfer from the heating zone Considering the differences in temperature drop at different positions inside the liner (*e g* , 12°C at the top and 0 5°C at the bottom part at an injection speed of 100 µl/min), the front of the liquid solvent film in the liner will be located nearer the exit of the liner Moreover, the lower the actual liner temperature the smaller is the evaporation rate It follows from the theoretical model (eqn 2) that in order to compensate for a temperature drop of 10°C, the injection speed has to be about halved

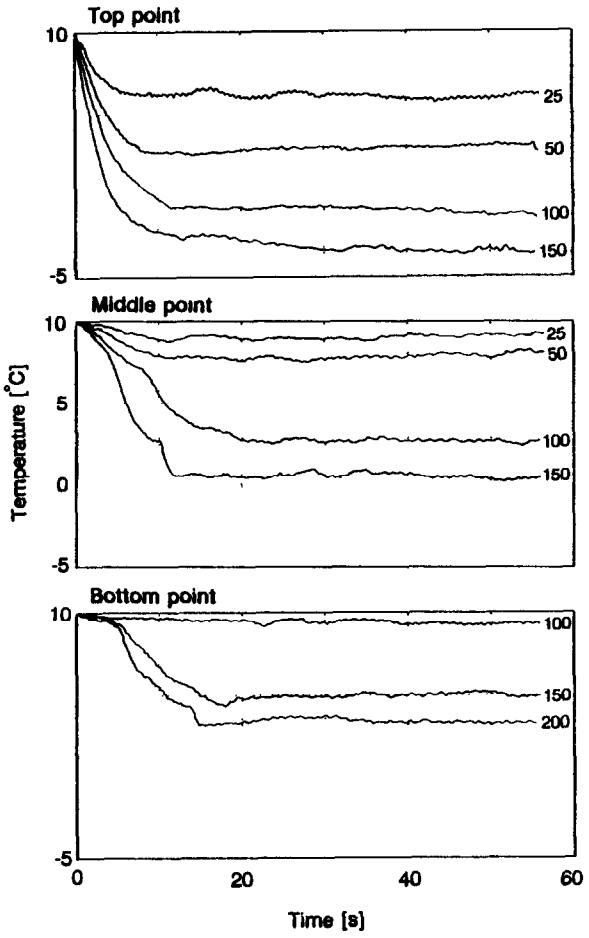

Fig 7 Temperature at different points inside the liner during solvent elimination for various injection speeds (numbers on the right-hand side indicate injection speeds in µl/min) Operating conditions initial liner temperature, 10°C, purge gas flow-rate, 620 ml/min, inlet pressure, 0 kPa

The magnitude of the cooling effect depends not only on the introduction speed of the sample, but will also depend on the heat of the evaporation of the solvent Values of the heat of evaporation for different solvents recalculated from the enthalpy of evaporation at the normal boiling point [25] are presented in Table III The heats of evaporation vary between 50 and 100 cal/ml for most of these solvents For the polar solvents used in reversed-phase LC, *i e* , methanol, acetonitrile and water, the heat of evaporation is significantly higher This means that, in order to vaporize identical volumes of

TABLE III

HEATS OF EVAPORATION OF SOLVENTS AT NORMAL BOILING POINT

Solvent	Heat of evaporation (cal/ml)	Solvent	Heat of evaporation (cal/ml)
n-Pentane	53	*n*-Hexane	53
Dichloromethane	104	Ethyl acetate	79
Acetone	95	Cyclohexane	66
Chloroform	88	Acetonitrile	143
Methanol	208	Water	540
Tetrahydrofuran	87	1,4-Dioxane	102
Diisopropyl ether	50		

methanol and *n*-pentane, four times more energy is required for methanol For water the difference is even more pronounced Compared with *n*-hexane water requires ten times more energy for complete vaporization Obviously, this also implies a different and much stronger cooling effect for methanol or water than for other solvents

Taking into account the effects of the operating conditions on solvent elimination discussed above, a representative chromatogram for a large-volume injection of sample A (*cf*, Table I) into a PTV injector is presented in Fig 8 The recoveries of the components of interest are dependent on their volatilities The more volatile components present in the sample (*n*-nonane, 2-octanone and *n*-decane) were largely lost However, components with volatilities lower than or similar to that of *n*-heptadecane were more than 90% trapped Selected operating conditions were preliminary optimized with respect to component recoveries Further optimization is required to achieve quantitative trapping of components in a liner of the temperature-programmed injector with large-volume sample introduction

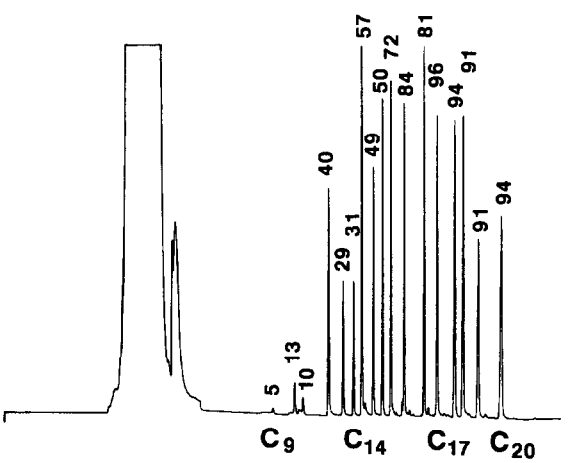

Fig 8 Chromatogram of a large volume of test sample A [numbers on the top of peaks indicate recoveries of components (%)], for peak identification see Table I Operating conditions sample volume, 150 μl, concentration, 0 08–0 16 ng/μl, injection speed, 20 8 μl/min, initial liner temperature, −20°C, purge gas flow-rate, 210 ml/min, inlet pressure, 5 kPa, additional purge time, 45 s, liner 2, column A

CONCLUSIONS

The temperature-programmed injector is an attractive sample introduction system for large sample volumes in capillary GC and it can also be used as an interface for on-line coupling of microbore and capillary LC and capillary GC

During the introduction of large sample volumes into a liner of the PTV injector the speed of sample introduction and solvent elimination rate have to be adjusted

The theoretical model allows the calculation of the solvent elimination rate (the maximum allowable speed of sample introduction) for large sample volumes for different solvents under given operating conditions assuming saturation of the purge gas with solvent vapour and an isothermal evaporation process For speeds of sample introduction up to about 50 μl/min the cooling effect during solvent evaporation inside the liner can be neglected Under operating conditions that allow a higher injection speed to be used, the speed of sample introduction can be reliably estimated

The solvent elimination rate can be significantly increased at increased purge gas flow-rates and a reduced pressure in the liner Moreover, owing to a reduced pressure in the liner during split solvent elimination, the amount of solvent entering the capillary column is significantly decreased

Enlargement of the gas–liquid contact area improves the process of saturation of the purge gas by solvent vapour, which is beneficial in the solvent elimination process

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