Sample introduction in high speed capillary gas chromatography : input band width and detection limits

Sample Introduction in High Speed Capillary Gas Chromatography; Input Band Width and Detection Limits

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Summary

The speed of analysis in capillary gas chromatography can be substantially increased by reduction of the column inner diameter. However, special demands are then posed upon instrumental design. In particular, the sampling system is highly critical because it has to be capable of delivering extremely small injection band widths which must be compatible with the column inside diameter. This study focuses on the evaluation of two potentially suitable sample introduction systems with respect to input band width and detection limits and their compatibility with small bore (≦ 100 μm) columns in capillary gas chromatography. One of them allows liquid on-column injection, based on liquid splitting, of only a few nl onto small bore (≦ 100 ◂m) fused silica columns. For gases, input band widths as low as 1 ms are obtained with this system. The other one is part of a miniaturized gas chromatograph with extremely low dead volume interfaces and detector volumes. It allows input band widths for gases of a few ms. Without any preconcentration ppm concentrations are measured in gaseous samples with a 80 ◂m thick film capillary column. It will be shown that a further reduction of the minimum detectable amount and analysis time is possible with this equipment.

1 Introduction

Theoretically the speed of analysis in capillary gas chromatography can be substantially increased by reduction of the column inner diameter. This approach was adopted by *Desty* [1] and later further investigated by *Gaspar et al.* [2,3] and *Schutjes et al.* [4]. The lack of compatible instrumentation is a serious obstruction to successful application of narrow bore columns (i.d. < 100 μm) in high speed capillary gas chromatography.

The required input band width of the sampling system (in the millisecond range) is one of the most critical factors, which must be carefully optimized in order to preserve a high column efficiency. On the other hand, introduction of the minimum detectable analyte concentration suggests the introduction of as large as possible a sample in view of the acceptable losses of column efficiency.

In this paper the effect of input band width on column efficiency and minimum detectable concentration is studied for two sampling systems suitable for high speed capillary GC. One of them is incorporated in a miniaturized gas chromatograph, in which all carrier gas and sample transport channels, valve seats, and a thermal conductivity detector are integrated on a three inch silicon wafer. The applicability and compatibility of the thermal conductivity detector, with an extremely small cell volume and negligibly low dead volume interfacing, for high speed capillary GC are discussed and evaluated.

The second system is basically an automated, pneumatically actuated high pressure valve with a sufficiently small loop and interfacing volume. In addition to the introduction of gaseous samples, this system can also be used for liquid on-column sample introduction.

The potential of both systems is illustrated by selected examples.

2 Theory

According to theory [4], analysis time (t_R) and thus peak width (σ_c) are directly proportional to the column inside diameter at high inlet to outlet pressure ratios. Therefore, for small bore ($d_c \leqq 100$ μm) and not too short ($l \geq 1$ m) capillary columns the peak width is proportional to the column diameter and analysis time ($\sigma_c \propto t_R$).

Assuming a negligible contribution to band broadening of interfaces, detector volume, and electronics, the apparent peak width (σ_t) only depends upon input band width (σ_i) and chromatographic peak broadening (σ_c):

$$\sigma_t^2 = \sigma_i^2 + \sigma_c^2 \qquad (1)$$

Substitution of $b = \sigma_i/\sigma_c$ in the plate height equation gives

$$N_t = \frac{N_{max}}{1+b^2} \qquad (2)$$

where N_t is the observed plate number and N_{max} the maximum (theoretical) plate number.

Dedicated to *Marcel Golay*, the inventor of capillary gas chromatography, on the occasion of his 85th birthday.

While chromatographic broadening of a peak is proportional to the analysis time ($\sigma_c \propto t_R$), it follows from eq. (2) that the input band width will also be proportional to analysis time for a defined or accepted loss in column efficiency ($\sigma_i \propto t_R$).

As shown by *Noij* and *Cramers* [5] for narrow bore columns with a high inlet to outlet pressure ratio ($p_i/p_o = p \gg 1$), at isothermal and optimum chromatographic conditions the minimum detectable analyte concentration for a defined (required) plate number can be expressed as:

$$C_{o(m)} = \frac{2}{\pi} \frac{R_n}{S} \frac{\sqrt{F(k)}}{D_{m,o}} \frac{\sqrt{1+b^2}}{b} \frac{1}{d_c} \quad (3)$$

for a mass flow sensitive detector, and

$$C_{o(c)} = \frac{4R_n}{S} \frac{\sqrt{1+b^2}}{b} \quad (4)$$

for a concentration sensitive detector without make-up gas.

$$F(k) = \frac{1+6k+11k^2}{3(1+k)^2} \quad (5)$$

In these equations R_n is the noise level, S the detector sensitivity, d_c the column diameter, k the capacity ratio of the compound, and $D_{m,o}$ the diffusion coefficient of the compound at the column outlet.

Obviously both column efficiency and minimum detectable concentration will decrease with increasing b values. While the minimum detectable concentration decreases more rapidly than the plate number, the optimum input band width will always be a compromise between column efficiency (and thus analysis time) and minimum detectable concentration. Therefore, in practical situations the acceptable input band width will be determined, in the first instance, by the required column efficiency and secondly by the minimum detectable concentration.

3 Experimental

A systematic study of the effect of a reduction of column diameter requires systems which are capable of delivering extremely small sample input band widths in order to be compatible with small bore columns. Two systems have been studied for this purpose. One is part of a miniaturized, microchip gas chromatograph [6]. The other one is a pneumatically actuated sampling valve, a slightly modified existing system in supercritical and liquid chromatography [9].

3.1 Micro GC

The miniature gas chromatograph (Microsensor Technology, Freemont, CA, USA) [6-8] is based on an etching technique called silicon micromachining, allowing carrier gas and sample channels, valve seats, and a thermal conductivity detector to be integrated on a three inch silicon wafer, which forms the basis of the GC module (**Figure 1**) [6].

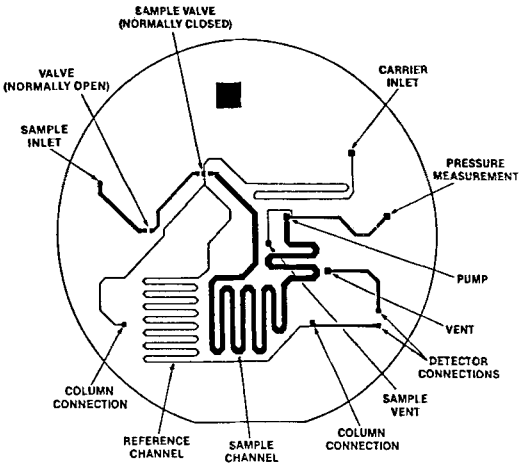

Figure 1

Schematic design of the silicon GC wafer.

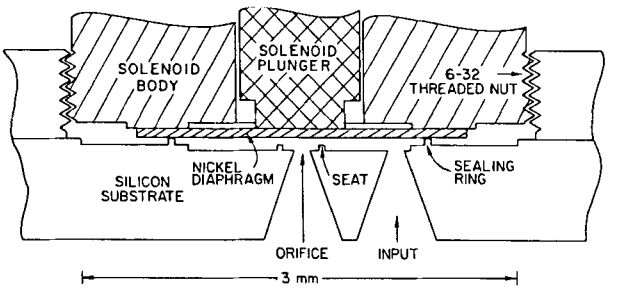

Figure 2

Cross-sectional view of the sample injection valve.

The capillary GC columns are mounted directly onto this wafer with ultralow dead volume seals. Due to negligibly small volumes of the compartments and interfaces, this micro GC is a nearly ideal instrument for use in high speed/narrow bore GC.

The entire unit used (Micromonitor 500, MTI, Freemont, CA, USA) can contain up to five complete gas chromatographs. It is provided with a self-contained computer which controls the portable gas analyzer, capable of determining and quantifying a wide variety of gases.

The miniature injection valve is a solenoid actuated diaphragm valve (**Figure 2**) [6].

The valve seats consist of a series of etched concentric ridges on the opposite side of the wafer to the gas channels. The nickel valve diaphragm is normally pressed against the seats by a small solenoid-driven actuator. When the valve is actuated the solenoid releases pressure from the diaphragm, allowing sample gas to flow over the valve

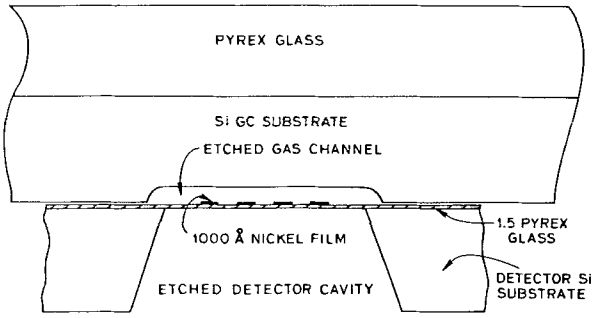

Figure 3

Cross-sectional view of the detector.

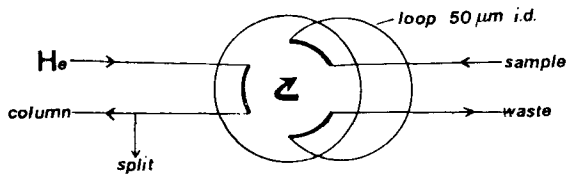

Figure 4

Schematic representation of valve connections.

seat and through a hole in the wafer to the carrier gas channel on the other side. The internal dead volume of the miniature valve is less than 4 nl.

At the start of the injection cycle, fresh sample gas is pumped by an external vacuum pump into the etched silicon channel which forms the sample loop. Next the inlet valve is closed and the sample gas is compressed. When the pressure reaches a preset value larger than the carrier gas pressure, in the standard equipment the injection valve is opened for 10 ms, injecting a plug of sample (without split) into the carrier gas stream.

The thermal conductivity detector is manufactured on a separate 5 mm square silicon chip, which is clamped against the main GC wafer (**Figure 3**). It forms the cover for an etched gas channel in the wafer leading from the output of the column.

According to the manufacturing specifications, the TCD cell volume is 1.5 nl and it has a *thermal* time constant of 200 µs. Due to the extremely low cell volume no make-up gas is needed. The sensing element is a thin film nickel resistor supported by a thin Pyrex glass membrane.

3.2 Actuated Sample Valve

The other sample introduction system studied for high speed GC uses a pneumatically actuated Valco 6-port valve (N6WT; Vici AG, Valco, Schenkon, Switzerland) with an internal rotor. The valve is mounted inside the oven of a Carlo Erba 4160 gas chromatograph. Carrier gas pressure is controlled with a Tescom 44-1100 high pressure-regulator. The various connections are schematically represented in **Figure 4**. The valve can be used at high temperatures (max. 350°C) and high pressures (max. 21 bar).

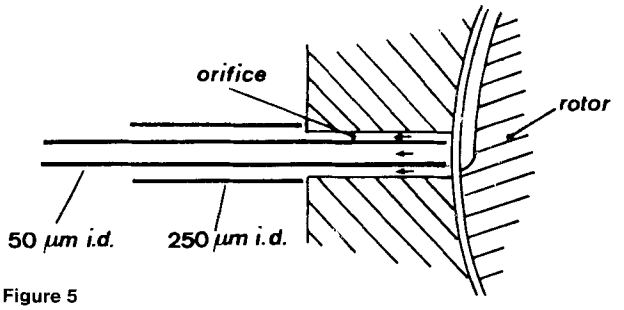

Figure 5

Positioning of the column in the valve.

The 50 µm i.d. analytical column is positioned inside a 250 µm i.d. capillary (**Figure 5**).

The 250 µm capillary ends at the orifice. The 50 µm capillary is pushed inside the orifice as close as possible to the rotor. To minimize the effect of dead volume still present the sample is split at the head of the column. Due to the rapid switching, only a small part of the contents of the sample loop is introduced. With this system, gas as well as liquid on-column injections are executed.

Since ordinary chartspeed recorders are far too slow, chromatograms using both systems were recorded on a digital storage oscilloscope (Nicolet 3091, Madison, WI, USA) capable of sampling at a maximum rate of 1 MHz or a Nelson Analytical/IBM-AT integration system (Nelson Analytical, Cupertino, CA, USA) capable of sampling at a rate of 100 Hz.

4 Results and Discussion

4.1 Microchip Gas Chromatograph

Input band width: Sample introduction was originally performed with the standard equipment. The injection valve actuation time (injection time) was fixed at 10 ms. In order to improve the flexibility in the selection of the input band width an electronic delay was installed so that the sample introduction period could be varied from 10-1000 ms in steps of 1 ms.

Simultaneously the pressure in the sample loop can be changed. Both these parameters injection time and sample loop pressure determine the injection profile and the sample size.

With a combination of a short (10 ms) valve opening time and a low injection pressure, the smallest input band width was obtained. The corresponding input band width (σ_i) was calculated to be approx. 3 ms. Corrections for column dispersion and the detector time constant are included in

this approximation. This is in good agreement with the theoretical value for the contribution of a plug injection to band broadening, according to the relation:

$$\sigma_i = \frac{\tau}{\sqrt{12}} \quad (6)$$

where σ is the actual width of the plug (τ = 10 ms in this case).

Injection profiles of methane at different sample loop pressures and injection times are shown in **Figure 6**.

Serious distortions of the methane peak shape due to overlap will be caused by pressure variations, an unavoidable effect of sample introduction in small bore columns. Therefore, in this experiment the TCD detector was replaced by a FID detector with a low time constant (≈ 1-2 ms). It is observed that with increasing input band width the injection profile approaches a rectangular shape. The values of the plug height calculated from the product of the known sample concentration, detector sensitivity and column flow are in fairly good agreement with experimental results.

The sample size is highly reproducible and corresponds to a standard deviation of about 1%.

High injection pressures and/or valve actuation times will result in pulses, which are observed at the beginning of the profile, as shown in Figure 6e. Most probably the column volume is too small for a complete expansion of the sample plug.

It follows from eqs. (2-4) that the relative contribution of the sample input band width to the overall bandwidth ($b = \sigma_i/\sigma_c$) has an effect on both column efficiency and minimum detectable analyte concentration. The ratio of input band width and chromatographic band width (b) can be calculated from injection profiles as shown in Figure 6.

Experimental data for peak height and plate number are presented for a thermal conductivity cell and a flame ionization detector as a function of b, in **Figure 7**.

The shape of the curves corresponds well to theory. It can be seen that a large gain in minimum detectable concentration can be expected when some loss in column efficiency is acceptable.

4.2 TCD Detector

Injection volumes were determined at different settings of sample loop pressures and injection times, by replacing the TCD by a calibrated FID. The TCD sensitivity ($\approx 5 \times 10^6$ Vcm^3g^{-1}) was then calculated from the slope of the plot of the TCD signal *versus* the amount of sample. Because the noise level was approx. 5 mV, it can be concluded that the signal-to-noise ratio is of the same order as that of a conventional TCD. In this way the minimum detectable concentration can be calculated at various experimental

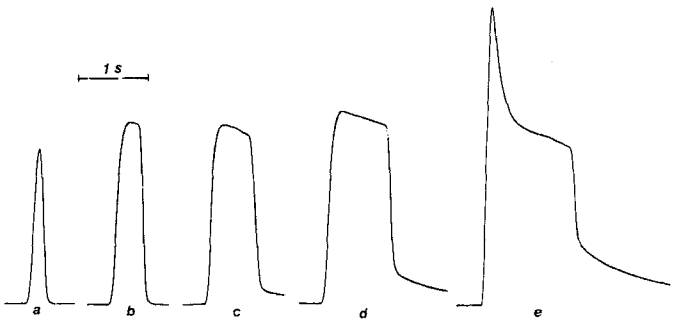

Figure 6

Injection profiles of methane at different sample loop pressures and injection times. Valve opening times: a) 70 ms, b) 110 ms, c) 160 ms, d) 210 ms, e) 305 ms.

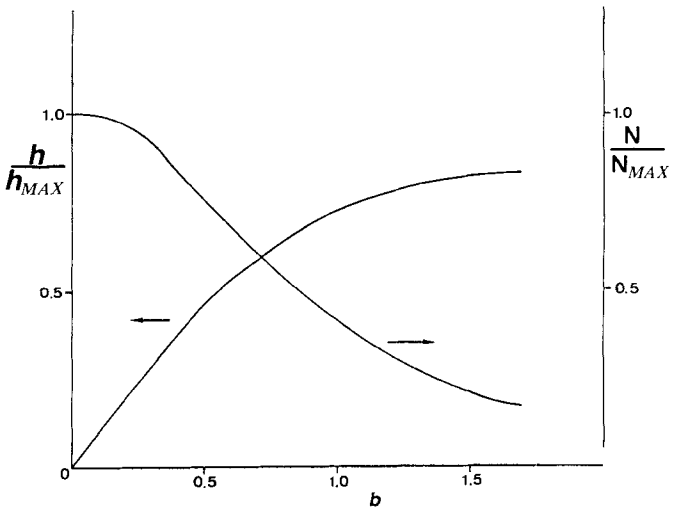

Figure 7

Representative plot of the relative peak height and apparent plate number *vs* b.

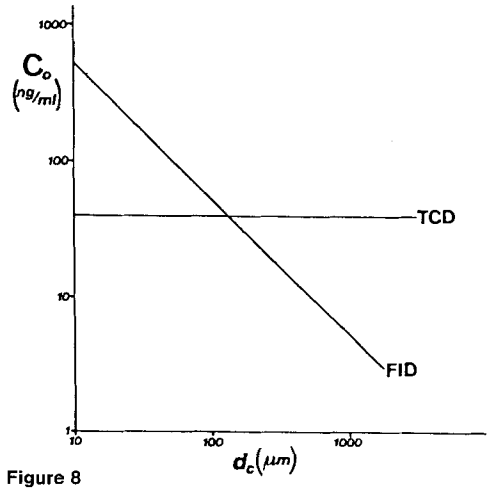

Figure 8

Plot of the minimum detectable analyte concentration (C_o) vs. column diameter (d_c). Experimental conditions: d_c = 80 μm; F_C = 3 μl.s^{-1}; b = 0.1; k = 4; $D_{m,o}$ = 3.10^{-5}m^2.s^{-1}; TCD: s = 5.10^6 [Vcm^{3}g^{-1}]; R_n = 5 mV; FID: s = 0.023 [cg^{-1}]; R_n = 3.5.10^{-13} A.

conditions so that optimization becomes possible. For instance, if b = 1 ($\sigma_i = \sigma_c$) a minimum detectable concentration for *n*-pentane was obtained of 1 ppm ($4 \times R_n$). This corresponds with a minimum detectable amount (W_o) of 3 pg (conditions $F = 3\ \mu l.s^{-1}$; $\sigma_t \cong 50$ ms).

In **Figure 8** the minimum detectable analyte concentration (C_o) is plotted as a function of column diameter for the TCD of the microchip gas chromatograph and an arbitrary FID. Obviously C_o is independent of column diameter for the TCD and inversely proportional to column diameter for the FID detector.

Conclusively, for column diameters below $\approx 135\ \mu m$ the application of a TCD detector with a sufficiently low dead volume becomes increasingly advantageous.

A great advantage of this particular TCD is its extremely low cell volume (1.5 nl), so that it can be used with narrow bore columns without addition of make-up gas.

Band broadening due to the detector cell volume is caused by spreading due to the laminar carrier gas flow and band broadening due to averaging of the detector signal over a gas volume corresponding with the effective detector volume, which may be smaller than the detector volume. The former contribution can be neglected because the cell volume is much smaller than the column volume. The latter contribution can be described as:

$$\sigma_d = \frac{V_{eff}}{F_c \sqrt{12}} \qquad (7)$$

where V_{eff} is the effective cell volume and F_c the column flow.

For an 80 μm column with a flow, $F_c = 3\ \mu l.s^{-1}$, the contribution to peak broadening of the detector was $\sigma_d = 0.14$ ms. Obviously this contribution to the overall peak broadening is negligible and allows a further reduction of column diameter without any problem.

As already pointed out by *Guiochon* [10] and *Schutjes* [11], considering the dynamic range and detection limits, a concentration sensitive detector is advantageous for narrow bore columns.

Another aspect in favor of a concentration sensitive detector is its column working range, being the range of the sample amounts in between the minimum detectable amount (Q_o) and the maximum sample amount that will not cause overloading (Q_s).

According to *Schutjes* [12] the working range (W) can be expressed as:

$$W = \frac{Q_s}{Q_o} \qquad (8)$$

As a result of this study and in agreement with the results reported by *Schutjes* [12], it can be concluded that the working range of a capillary column with a high inlet-to-outlet pressure ratio ($P \gg 1$), for a mass flow sensitive detector respectively a concentration dependent detector is proportional to d_c^2 or d_c respectively. This means that the decrease in working range for a concentration sensitive detector is considerably less than for a mass flow sensitive detector.

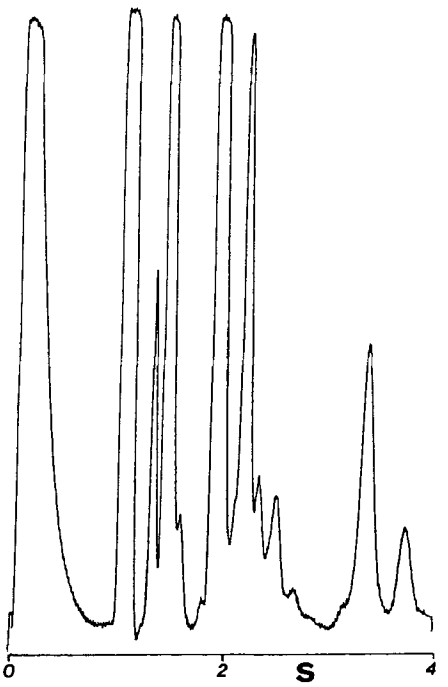

Figure 9

High speed chromatogram of gasoline head space; column. i.d. = 80 μm; l = 1 m; d_f = 0.4 μm; stationary phase is phenylmethyl silicone, carrier gas He.

4.3 Actuated Sample Valve

Gaseous samples: In order to minimize the effect of dead volume still present a split ratio of approx. 1:50 was used. Due to compression of the gaseous sample in the loop, a certain minimum switching time appeared to be required in order to transfer some sample into the column.

In order to investigate the limitations of the input band width with this sampling valve, an amount of a *n*-pentane headspace sample, corresponding with the smallest possible peakwidth, was injected onto a non-coated 50 μm fused silica column. The resulting chromatogram is presented in **Figure 10**.

A peak width corresponding with a standard deviation of $\sigma_t = 2.0$ ms was obtained. Neglecting the contribution of dead volumes in the detector and interfaces as well as the effects of peak deformation caused by time constants in the registration system, an input band width of 1.3 ms is obtained, while the chromatographic peak broadening in this experiment was 1.5 ms.

The contribution of other factors such as the time constant of the detector amplifier ($\sigma_{el} \approx$ 1-2 ms), detector volume

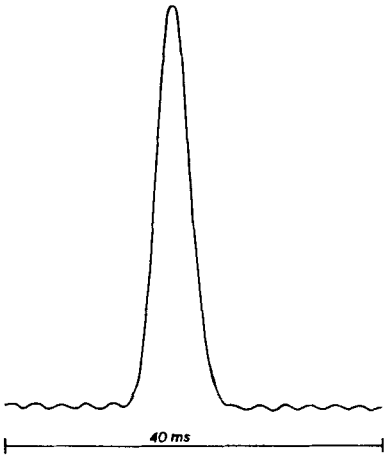

Figure 10

Peak profile of a *n*-pentane peak. Sample: *n*-pentane headspace. Column: non-coated fused silica, i.d. = 50 μm, *l* = 1 m; p_i = 10 bar; detector: FID; carrier gas He.

($\sigma_d \approx$ 1-2 ms; flow 100-200 ml. min^{-1}) can only be estimated. Therefore, the actual input band width cannot be obtained with a sufficient accuracy.

Nevertheless, the minimum input band width that can be obtained for gaseous samples will definitely be below 1 ms.

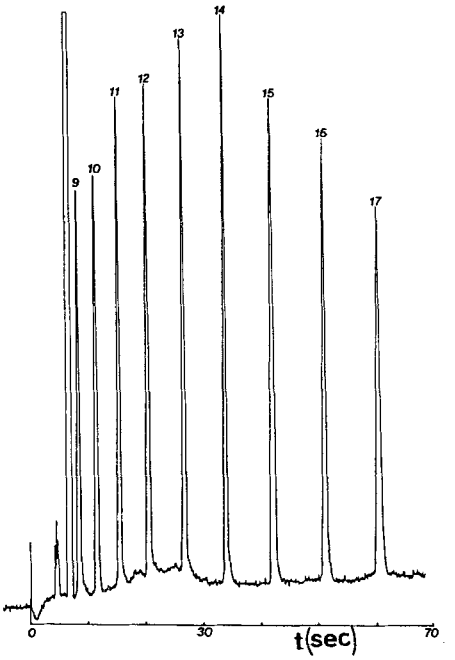

Figure 11

On-column injection of a 0.1% (v/v) solution of *n*-alkanes (C_9-C_{17}) in dichloromethane. Column: *l* = 4 m, i.d. = 50 μm, stationary phase: cyanopropylpolymethylsilicone (60% CN), d_f = 0.1 μm.

4.4 Liquid On-Column Injection

Some preliminary experiments were executed to test the applicability of the pneumatically actuated sample valve for liquid on-column injection on small bore (< 100 μm) capillary columns. To avoid dead volume problems at the interface between the valve and the column, liquid splitting (split ratio 1:10) was used at the head of the column.

A preliminary representative example of this injection technique is shown in **Figure 11** for a mixture of *n*-alkanes in dichloromethane (0,1% v/v).

Although these results need further optimization, it appears possible to introduce a few nl of a liquid sample onto narrow bore capillary columns. New results on aspects as reproducibility, discrimination, optimization, *etc.*, will be published elsewhere [9].

5 Conclusions

Extremely small input band widths (≦ 3 ms) are obtained, which are compatible to a high extent with narrow bore (< 100 μm) columns in capillary gas chromatography. With the pneumatically actuated sample valve liquid on-column injection of only a few nl is possible.

The effect of an accepted loss in column efficiency on the minimum detectable concentration is demonstrated. It is shown that the minimum detectable concentration is independent of column diameter for a TCD detector and inversely proportional to the column diameter for the FID detector. For columns with a diameter below 135 μm, without addition of make-up gas, a TCD detector is the best choice.

The microchip gas chromatograph described in this study is highly suitable for high speed capillary GC with narrow bore columns. This is due to extremely low dead volumes of the interfaces and the detector (1.5 nl), the time constants due to detector volume and electronics, and minimum detectable concentrations for narrow bore capillary columns.

In addition, it allows a substantial decrease of column diameter and thus analysis time.

Acknowledgment

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