Sample enrichment in high speed narrow bore capillary gas chromatography

Sample Enrichment in High Speed Narrow Bore Capillary Gas Chromatography

A. van Es, J. Janssen, C. Cramers, and **J. Rijks***
Laboratory of Instrumental Analysis, Eindhoven University of Technology, Department of Chemical Engineering, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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Summary

Reduction of the column diameter has proved to be a highly efficient tool to increase the speed of analysis. Unfortunately, the requirements for instrumental design with respect to sample input band width, low dead volume interfacing, and time constants of detection and registration systems are the more critical the smaller the inside diameter.

Recently we reported input band widths as low as 1 ms [1] for gaseous samples at ppm concentration levels, without any preconcentration, in a study with narrow bore columns and thermal conductivity detection.

In this study a simple versatile micro on-column cold trap/thermodesorption enrichment system for narrow bore columns is introduced and evaluated. The combination of considerable sample enrichment and preservation of the compatibility of the required input band width with column dimensions is critically examined. The process of thermodesorption (reinjection) which is the most critical step, is particularly emphasized.

The system consists of a short aluminum coated fused silica or metal capillary with a low mass and a low cost electrical heating. Input band widths down to 1 ms are obtained without extreme demands on electrical power (300 watt). The potential of the system is illustrated with some extremely fast separations.

1 Introduction

According to theory, reduction of the column diameter can substantially increase the speed of analysis. This approach was adopted by *Desty* [2] and later further investigated by *Gaspar et al.* [3,4] and *Schutjes et al.* [5,6]. However, the lack of compatible instrumentation has seriously obstructed the application of narrow bore columns (< 100 μm). Especially the sampling system is a critical factor because the input band width must be extremely low (in the millisecond range) to preserve a high column efficiency.

Recently we have reported two systems capable of obtaining input band widths as low as 1 ms [1] for gaseous samples at ppm concentration levels without any preconcentration. For a further decrease in minimum detectable concentrations preconcentration is necessary. However, simultaneously a narrow input band width must be preserved. Therefore a micro on-column cold trap/thermodesorption system was developed.

This study focuses on instrumental and experimental factors which determine the input band width. It will be shown that the system provides a simple versatile and efficient sample introduction and enrichment system for high speed narrow bore capillary gas chromatography. This is illustrated by some examples.

2 Theory

It is evident that in high speed gas chromatography high demands are posed upon the injection band width. In a previous paper [1] we have shown that, for a given plate number and a high pressure drop, the injection band width (σ_i) is proportional to the analysis time t_r and column diameter d_C:

$$\sigma_i \sim t_R \sim d_C \qquad (1)$$

Using a cold trap/thermodesorption system σ_i is determined by the length of the condensed zone and the evaporation rate. The principle of cold trapping is a reduction in migration speed due to an increase in capacity factor. Considering the trapping as a chromatographic process the migration speed is reduced with a factor $R = 1/(1+k)$, where k is the capacity factor at the cold trap temperature. Consequently the introduced band width, which is focused in the cold trap, is reduced by a factor R. The total reinjection band width can now be expressed as:

$$W_i = V_s / (F_c{}^*R) + t_v \qquad (2)$$

where

W_i = reinjection band width (temporal units)
V_s = sample volume before trapping
F_c = column flow
R = relative migration speed
t_v = vaporization time

Provided that no saturation of the gas phase occurs the vaporization time will only depend upon the heating rate of the trap. Neglecting heat loss, the trap temperature for an electrically heated trap as a function of time (T(t)) can be written as:

$$T(t) = \int_0^t \frac{I^2(t) \cdot R(t)}{m \cdot C(T)} \cdot dt + T_o \qquad (3)$$

where

I(t) = heating current
R(T) = and C(T) are temperature dependent resistance and heat capacity
m = mass of the trap
T_o = initial temperature

Besides a high electrical power, a low mass of the trap is essential for a rapid evaporation.

Apart from the possibility of obtaining a compatible band width for narrow bore columns, cold trapping has the advantage of acquiring substantially lower minimum detectable concentrations. *Noij* and *Cramers* [7] have reported expressions for the minimum detectable concentrations in the case of direct injection without trapping. From eq. (2) it can be seen that if the vaporization time is negligible their concept can also be extended to cold trapping. The only difference is the introduction of the factor R which denotes the degree of focusing of the introduced band width.

Under isothermal and optimum chromatographic conditions the minimum detectable concentrations (C_o) for cold trapping can then be written as:

$$C_o(c) = \frac{4 R_n}{S} \cdot \frac{\sqrt{1+b^2}}{b} \cdot R \qquad (4)$$

for a concentration sensitive detector and,

$$C_o(m) = \frac{2}{\pi} \cdot \frac{R_n}{S} \cdot \frac{\sqrt{F(k)}}{D_{m,o}} \cdot \frac{\sqrt{1+b^2}}{b} \cdot \frac{1}{d_c} \cdot R \qquad (5)$$

for a mass flow sensitive detector. Where:

R_n = the noise level
S = sensitivity
σ_c = chromatographic peak broadening
σ_i = input band width
$b = \sigma_i / \sigma_c$
$F(k) = (1 + 6k + 11k^2) / (3(1 + k)^2)$
$D_{m,o}$ = solute diffusion coefficient in the mobile phase at the column outlet.

As can be seen, reduction of the column diameter gives no loss in minimum detectable concentration for a concentration sensitive detector. This only holds if the detector volume is compatible with the column dimensions. In a previous study [1] it was experimentally shown that, in agreement with a recently published theoretical model [7], for columns with a diameter < 130 µm TCD detection has to be preferred above a FID for low concentrations (C_o). A TCD with an internal volume of 1.5 nl was used for this study (MTI, Freemont, Ca, USA).

The factor R can be very low (*e.g.* 10^{-5}) [8,9]. According to eq. (4) and (5) this enables trace analysis (ppb-ppt range), while according to eq. (2) at the same time a narrow input band width can be obtained, if the heating rate is sufficiently large.

3 Experimental

The on-column cold trap reinjection system is schematically presented in **Figure 1**. An aluminum coated fused silica capillary (L = 10 cm, i.d. = 200 µm, mass = 10 mg) surrounds the separation column (50 µm i.d.). In order to establish optimal electrical contact the leads were connected to the aluminum coated capillary with graphite ferrules and brass unions.

Approximately 2 cm of this trap was cooled by nitrogen gas which was chilled by forcing it through a dewar with liquid nitrogen. The flow of cooling gas was not interrupted during the heating step.

The heating circuit is schematically presented in **Figure 2**. The timer circuit, adopted from *Hopkins* and *Pretorius* [10] delivers a current pulse (ac) of 10-50 ms. The desorption voltage can be set at transformer 1. With transformer 2 the voltage decreases and the current increases with a factor 17.

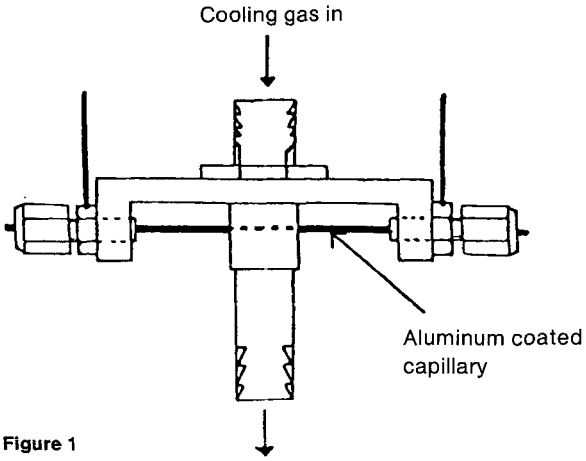

Figure 1

Schematic representation of the cold trap reinjection system.

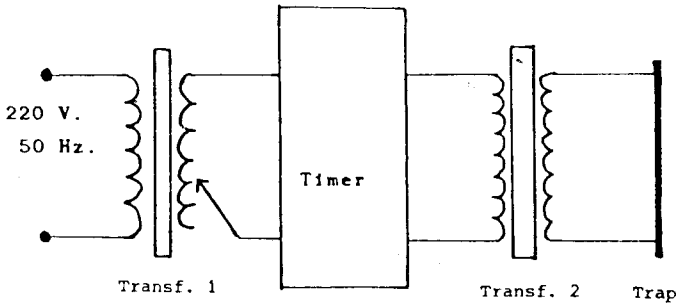

Figure 2

Schematic representation of timer circuit.

The cold trap reinjection system including the separation column were mounted in a Carlo Erba Fractovap 4160 gas chromatograph with FID detection. Carrier gas pressure was regulated with a Tescom 44-1100 high pressure regulator. Before trapping the sample was introduced by split injection.

Since ordinary chartspeed recorders are far too slow, chromatograms were recorded with a digital storage oscilloscope (Nicolet 3091, Madison, WI, USA) capable of sampling at a maximum rate of 1 MHz.

4 Results and Discussion

The critical step in a cold trap/thermodesorption system for high speed capillary GC is the reinjection of the trapped sample. The thermal mass of the trap must be as low as possible. At first it was attempted to coat a short section of the capillary column with electrically conductive paint, but this paint could not withstand the required high heating rates. Since then an aluminum coated fused silica column was used for resistance heating of the cold section. This type of column was recently developed for high temperature GC.

4.1 Heating Rate during Thermodesorption

A heating rate of the thermodesorption cold trap of 27000°C/s was calculated from eq. (3) (m = 15 mg, C = 0.8 J/g/°, applied voltage 9 V, P = 325 W). With a low mass thermocouple (d = 15 μm, m = 1 mg) placed inside the column a heating rate of 4000°C/s is observed experimentally during a current pulse of 50 ms. The thermocouple signal was recorded with a digital storage oscilloscope after amplification with a fast amplifier. The resulting temperature profile is presented in **Figure 3**.

Due to the restricted speed of heat transfer through the column wall, the maximum temperature is reached after 80 ms. Since the cooling has not to be switched off during heating, a next analysis can be performed after a few seconds. The discrepancy between calculated and experimental data can possibly be caused by an increase of the thermal mass due to ice deposition on the trap, a non-

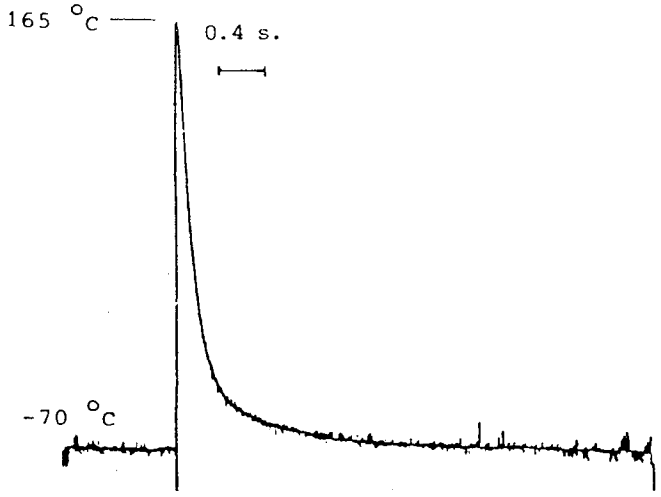

Figure 3

Temperature profile measured inside the capillary cold trap. Heating voltage: 10.5 V, 50 Hz pulse time: 50 ms.

negligible heat loss of the trap and the connecting leads and a temperature gradient across the trap diameter.

4.2 Effect of Applied Voltage and Pulse Time on Peak Profile

The profiles of the peaks after thermal desorption depend upon the deposition profile, the thermal mass and electrical resistance of the trap, the applied voltage, and the pulse time. The effect of the applied electrical power on the peak profile after thermal desorption is shown in **Figures 4** and **5**.

It can be concluded that at a voltage > 9 V the effect of evaporation is negligibly small compared to the contribution of other sources of peak broadening, notably the length of the condensed zone and chromatographic and instrumental peak broadening (*e.g.* dead volume in detector and time constants).

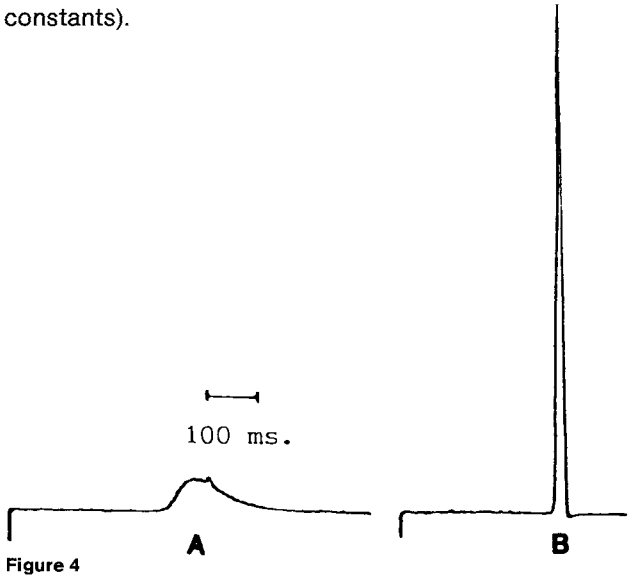

Figure 4

Reinjection profile of *n*-octane at different heating voltages. Column: 0.7 m, 50 μm uncoated. Cold trap: T = −70°C. A) 7.65 V; B) 10.3 V (50 ms pulse).

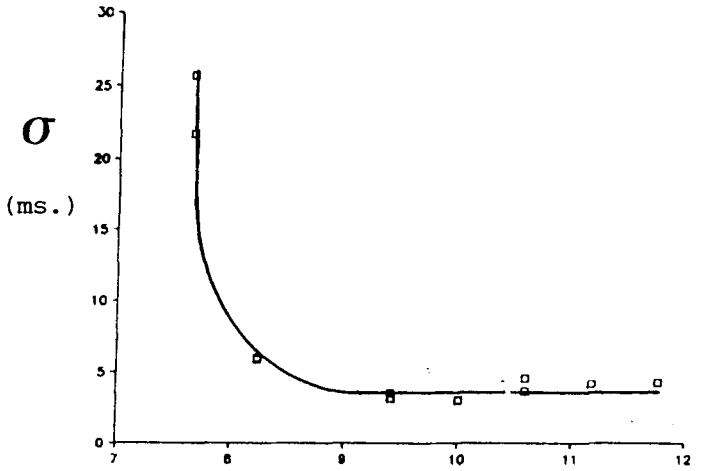

Figure 5

Standard deviation of reinjected *n*-C9 as a function of heating voltage.

The effect of pulse time on peak shape is demonstrated in **Figure 6**. Obviously the maximum trap temperature is decreased at shorter pulse times, so that the solutes get insufficient mobility. This will result in a leading and broadened peak profile as can be seen in Figure 6A. Beyond a minimally required pulse time symmetrical narrow peaks are obtained as illustrated in Figure 6C.

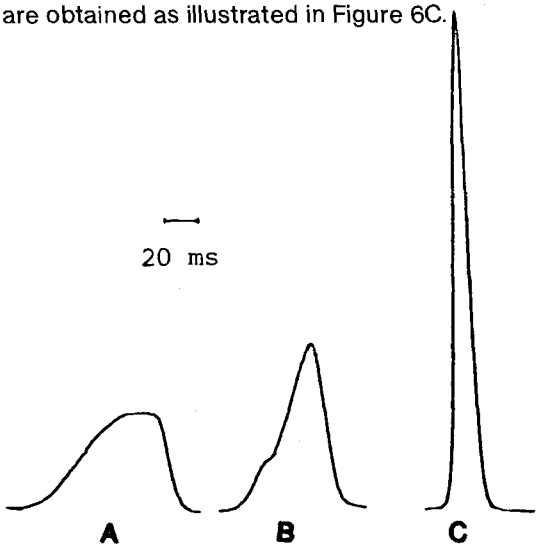

Figure 6

Effect of pulse time on reinjection profile, A = 10 ms, B = 20 ms, C = 50 ms. Column: 0.2 m, 50 μm. Carrier gas: He, 4.5 bar. Sample: *n*-C10. T(trap) = -72°C, heating voltage: 11 V.

4.3 Effect of Sample Size on Peak Shape

Different phenomena may cause overloading of the trap due to the high speed of heating [11]. The first one is concentration overloading: too high a concentration in the mobile phase. The capacity factor becomes dependent on concentration resulting in a leading peak profile. The second is peak broadening due to volume overloading caused by instantaneous evaporation of a large sample amount. This effect may be partially compensated because the heating rate of the trap may result in a reduced evaporation speed due to gas phase saturation.

The effect of the sample size on peak width and peak shape is illustrated in **Figure 7**. The cold trap/thermodesorption device was directly coupled to the detector which corresponds to an effective length from the center of the trap to the flame tip of 14 cm. The peak widths of both the peaks 7A and 7B, which show a good symmetry, correspond to a standard deviation of 1.49 ms. At larger sample amounts a leading peaks shape and peak broadening appear. Discrimination between concentration and volume overloading was not possible at this moment. That these results are obtained with non-coated columns suggests that sample sizes up to 10 ng/component will not seriously harm column efficiency for coated columns.

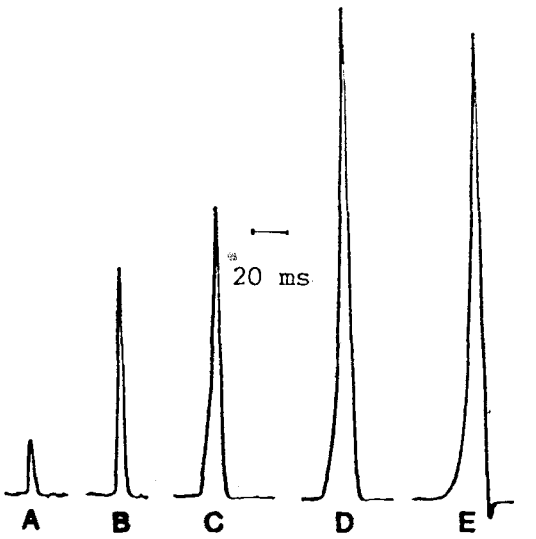

Figure 7

Effect of sample amount on reinjection profile. A = 0.24 ng; B = 0.96 ng; C = 3.36 ng; D = 9.6 ng; E = 24 ng. Column: 50 μm i.d., sample: *n*-C9, heating: 11 V, 50 ms.

4.4 Estimation of Input Band Width

The chromatographic band broadening can be calculated from the *Golay-Giddings* plate height equation. The rule of additivity of variances for various effects that contribute to the apparent peak width, in principle allows the estimation of the input band width.

As shown in **Figure 8A** the *n*-nonane peak has a standard deviation of 1.49 ms. The contribution of the detector electronics can be neglected (amplifier rise time (0-90% fs) = 3 V/ms). Whether peak broadening due to dead volume in the flame can be neglected is not yet clear.

A calculated chromatographic broadening (σ_c = 0.96 ms) of the column connecting the trap and detector (L = 14 cm, i.d. = 50 μm, k = 0) yields an injection band width of 1.1 ms. Obviously the reinjection band width is highly compatible with high speed narrow bore capillary GC.

The reinjection profile of *n*-dodecane (**Figure 8C**) on a coated OV-1 capillary column (L = 0.15 m, i.d. = 50 μm) shows that also components with higher boiling points can be accepted without any problem.

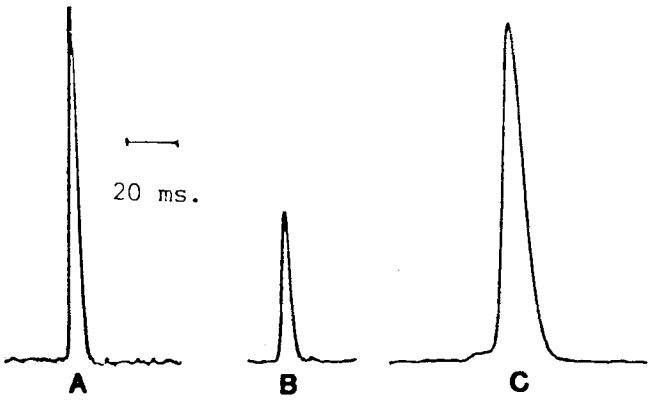

Figure 8

Some reinjection profiles. A) 0.96 ng *n*-C9, 50 μm uncoated column, T(trap) = −75°C, heating: 11 V, 50 ms. B) 0.6 ng *n*-C10, 50 μm uncoated column, T(trap) = −95°C, heating: 12 V, 50 ms. C) *n*-C12, 50 μm column coated with OV-1, T(trap) = −77°C, heating: 11 V, 50 ms.

4.5 Preseparation in the Cold Trap

Preseparation will occur to some extent in any cold trap [12]. Differences in capacity ratio will result in a deposition at different spots in the cold trap due to the existing temperature gradient. The more volatile solutes will proceed further with the direction of carrier gas flow. Components with a higher capacity factor will be focused more close to the inlet of the trapping column. The desorption which can principally be considered as a temperature programmed separation in a short column with a high programming rate will also enhance separation.

The effect can be demonstrated if separation outside the cold trap is eliminated, *e.g.*, by directly coupling the trap to the detector (250°C). A representative preseparation of *n*-alkanes is shown in **Figures 9A** and **B**.

4.6 Some High Speed Separations

The potential of the cold trap/reinjection system will be demonstrated here by some examples of high speed

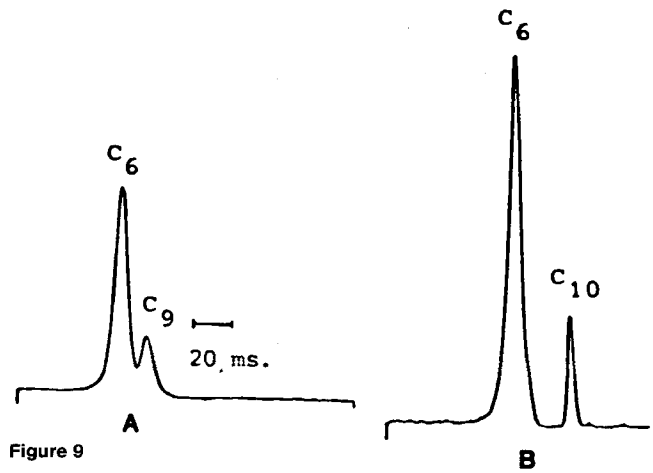

Figure 9

Preseparation in the cold trap. A) *n*-C6 and *n*-C9; B) *n*-C6 and *n*-C10, 50 μm capillary coated with OV-1, L = 0.14 m, T(trap) = −74°C, heating: 11 V, 50 ms.

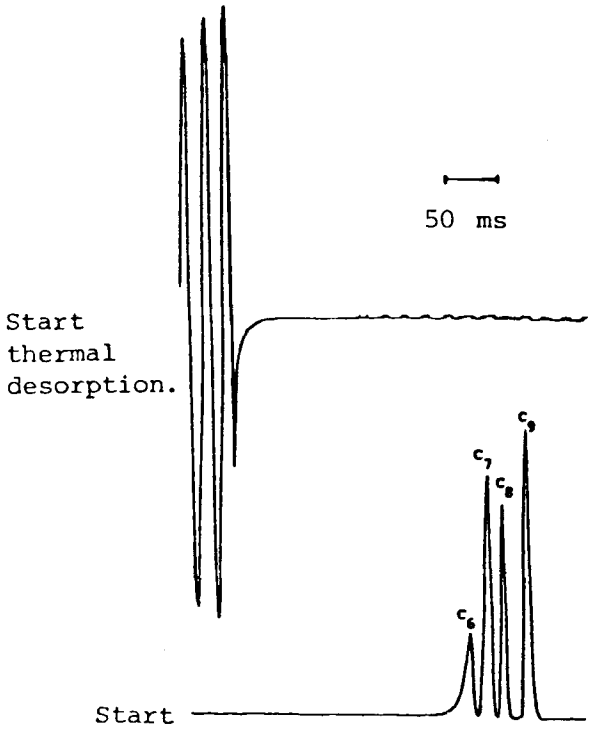

Figure 10

High speed separation of *n*-C6 to *n*-C9. Upper part: applied heating voltage. Column: 50 μm uncoated fused silica, L = 0.35 m, T = 70°C, Carrier gas: He, 4.5 bar, T(trap) = −70°C, heating: 11 V, 50 ms.

separations. In **Figure 10** the separation of an *n*-alkane mixture (C6-C9) is shown with an uncoated fused silica capillary (L = 0.35 m, i.d. = 50 μm). In this case separation takes place by adsorption onto the column wall. The chromatogram is triggered by the applied voltage pulse which is also presented in Figure 10.

In **Table 1** the measured and calculated peak widths of the components are given. The differences are small which corresponds with an already estimated injection band width of 1 ms.

Table 1

Measured (Figure 10) and calculated standard deviations.

Component	Measured σ_t [ms]	calculated σ_t [ms]	retention time [ms]
n-C6	3.48	2.5	245
n-C7	2.97	2.6	293
n-C8	2.12	2.6	307
n-C9	2.80	2.8	332

A representative example of a high speed separation of some hydrocarbons on a OV-1 coated fused silica capillary column (L = 0.3 m, i.d. = 50 μm) is shown in **Figure 11**. The corresponding retention times and standard deviations of the components are given in **Table 2**. The larger standard deviation of *n*-hexane is due to insufficient focusing at the applied trapping temperature.

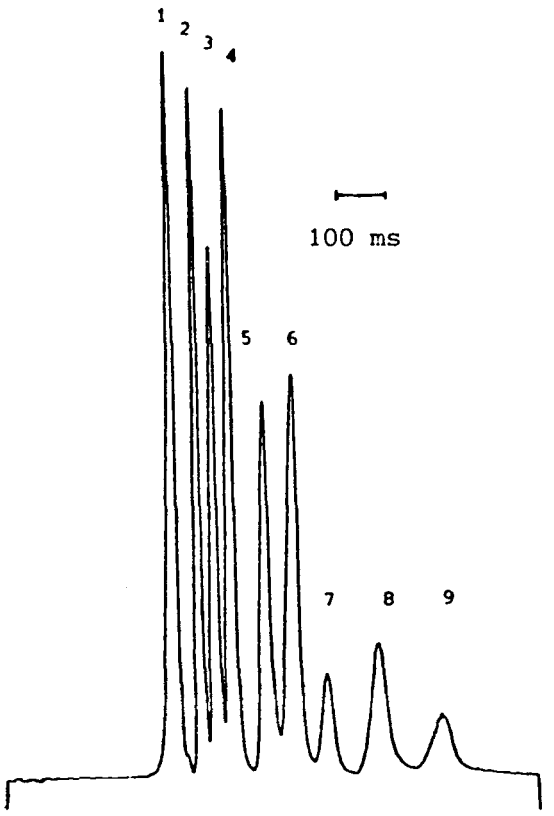

Figure 11

High speed chromatogram of some hydrocarbons. Column: 50 μm coated with OV-1, L = 0.3 m, T = 72°C. Carrier gas: He, 4.5 bar. T(trap) = −75°C, heating: 11 V, 50 ms.

The total separation of the nine components was finished within 660 ms after starting the thermal desorption. For cyclohexane (k' = 0.2) 24000 plates per second are generated. To our knowledge this is one of the fastest separations ever published. (*Jonker et al*, [13]: 4 peaks in 150 ms, 650 plates, with a short packed column; *Desty* [2]: 15 components in about 2s).

5 Conclusions

With the developed cold trap/reinjection system injection band widths down to 1 ms can be obtained, which is highly compatible with high speed narrow bore capillary GC. Extremely fast separations are possible while simultaneously a high sample enrichment can be obtained allowing trace analysis.

Table 2

Retention times and standard deviations of components from Figure 10.

No.	Component	Retention time [ms]	σ_C [ms]
1	*n*-C6	255.8	4.92
2	Cyclohexane	291.8	3.48
3	*n*-C7	316.0	4.33
4	Methylcyclohexane	342.6	4.67
5	Toluene	392.6	5.69
6	*n*-C8	436.8	7.65
7	1,2-Dimethylhexane	483.0	7.90
8	Ethylbenzene	564.2	11.0
9	*n*-C9	660.4	13.7

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